SOLVENT EXTRACTION OF GEORGIA PINE NEEDLES

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SOLVENT EXTRACTION OF GEORGIA PINE NEEDLES

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INTRODUCTION

Lumbering, turpentining, and other operations involving the long-leaf pine (pinus palustris) found in Georgia and other southern states are important industries and provide employment for a large number of people. In fact, the extent of these operations is such that they have a considerable influence on the economy of the Southeast. Therefore, any successful attempt to utilize by-products from these industries would be beneficial to the economy of this section of the country.

At the present time, pine needles obtained from lumbering operations are discarded. In the attempt to find a usefor these needles, it was decided to investigate the possibility of obtaining essential oils and other products from them. Some preliminary work[1] was done at the Georgia Institute of Technology on the extraction of essential oils from the needles by steam distillation. Only a trace of oil was obtained in that investigation. The possibility of obtaining an industrially important product by steam distillation appeared so remote that that method was discarded as not being worthy of further study.

The object of this investigation was to study the possibility of removing soluble materials from Georgia pine needles using various volatile solvents. The effect of different solvents on extraction rate

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[1] Daniel, L. R., Personal communication.

and the percent product extracted was studied. In addition, the possibility of obtaining the more volatile essential oils by vacuum fractional distillation of the extracted material was investigated. The results presented in the body of this thesis show that a considerable amount (as much as 9% by weight) of material can be extracted from pine needles with volatile solvents, and small quantities of essential oils can be separated from the extract by vacuum fractional distillation.

TERPINES

Essential oils have been defined as volatile oils from plant origin.[2] These oils may be classified into four main groups of chemicals;[3]

1. Terpines
2. Straight chain compounds without side branches
3. Derivatives of benzene
4. Miscellaneous

The terpines and terpine derivatives are the principal constituents of most essential oils. The terpines are a family of compounds with the basic formula $C_{10}H_{16}$ and may be either open-chain or cyclic in structure. In a broader sense, the term terpine is extended to include the hemiterpines, C_5H_8; the sesquiterpines, $C_{15}H_{24}$; the diterpines, $C_{20}H_{32}$; and polyterpines $(C_5H_8)_n$. Most of the terpines are colorless liquids with boiling points between 155° C and 185° C, but a few are solids. They have characteristic odors and many of them are optically active. Due to the presence of double bonds, some of this class of compounds are quite active chemically. They take part in both addition and polymerization reactions.[4]

Pine-needle oils contain a fairly large percent of terpines. Sandermann[5] reports that the leaf oil of the Pinus Sylvestris consists

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[2]Guenther, E.; The Essential Oils, Vol. I, D. Van Nostrand Company, New York, 17 (1948).

[3]Ibid; p. 18.

[4]Wertheim, E.; Textbook of Organic Chemistry, Blakiston Company, Philadelphia, 622 (1945).

[5]Chemical Abstracts; 31, 2532[3] (1940).

of over 60% terpines, and Lehman and Lynn[6] found the leaf oil of the Juniperus Scopulorum to contain about 42% terpines. Other references[7,8] indicate the predominance of terpines in needle oils from different pine species.

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[6]Lehman, A. J., and Lynn, E. V.; "The Leaf Oils of Washington Conifers: II. Juniperus Scopulorum", Journal of the American Pharmaceutical Association, 19, 1071 (Oct. 1930).

[7]Parry, E. J.; The Chemistry of Essential Oils and Artificial Perfumes, Scott, Greenwood and Son, London, 53-60 (1921).

[8]Wahlenberg, W. G.; Longleaf Pine, Charles Lathrop Pack Forestry Foundation, Washington, 24, 25 (1946).

COMMERCIAL SOLVENT EXTRACTION OF ESSENTIAL OILS

Essential oils in general are produced commercially by steam distillation, extraction with hot fats (maceration), extraction with cold fats (enfleurage), and by extraction with volatile solvents.[9] In relatively small quantities, many of these oils find use in perfumes or in flavoring extracts. However, some, such as oil of turpentine, find wide use in paint and allied industries. Steam distillation is the method which has been most used to obtain essential oils, but as this paper deals with solvent extraction, only solvent extraction methods will be discussed.

Extraction of plant material is usually carried out by batch extraction with each batch being treated with solvent three or four times. Washings from the third extraction of one charge are used for the second extraction of another charge, etc. Figure 1 shows a schematic diagram of a volatile solvent extraction system.[10]

After the plant material has been extracted to the extent desired, it contains a considerable amount of solvent. Water-insoluble solvent clinging to the mass of plant material is recovered by blowing live steam into the extractor and condensing the steam and steam-distilled solvent in the solvent recovery condenser. The water is drawn off in the decanter, and the solvent is returned to the fresh solvent tank.[11] If the solvent used is water soluble, it can be removed by

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[9] Guenther; op. cit., p. 85 ff.

[10] Ibid; p. 207

[11] Ibid; p. 207

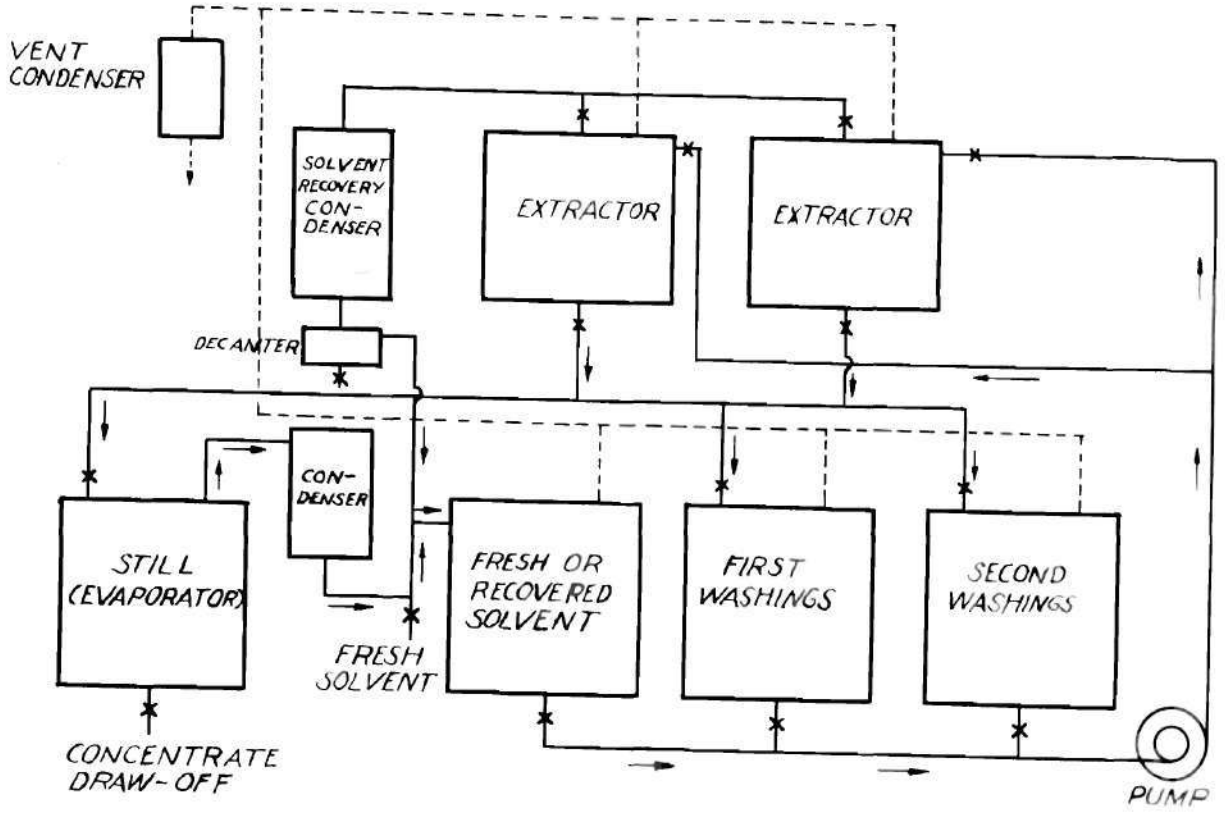

FIGURE 1: SCHEMATIC DIAGRAM OF A VOLATILE SOLVENT EXTRACTION SYSTEM

distilling with hot air instead of steam; or the extractor can be jacketed, heated indirectly by steam, and the solvent driven off and condensed.

Two types of extractors are currently used: stationary and rotary. The stationary extractors consist of vertical cylindrical tanks which contain perforated metal grids supported by a central shaft. The plant material is charged upon these grids, and the extractor is closed with a metal cover fastened with clamps. The rotary Garnier type extractor consists of a cylindrical drum divided into four perforated

partitions, Figure 2.[12] This drum rotates on a hollow axle which provides the inlet for the solvent and also for the steam to remove the solvent remaining after extraction is completed. Plant material is

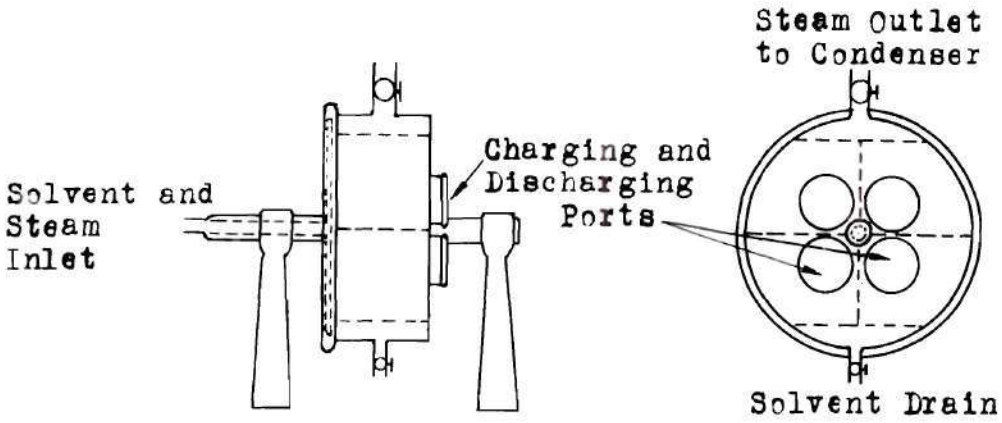

FIGURE 2: ROTARY EXTRACTOR, GARNIER TYPE

charged into the extractor through four ports located on one side. The extractor is run only partially filled with solvent. The rotating drum causes the material to be slowly dipped into and out of the solvent. The rotary extractor requires less solvent than does the stationary extractor, hence solvent losses are smaller. The rotary motion provides better contact between plant material and solvent, thus percentage extraction is higher with the Garnier extractor. However, for some uses, especially when the material to be extracted is quite voluminous, the stationary extractor is preferred.[13]

After extraction is completed, the solvent must be removed from the extract. Most of the solvent is driven off in a still operated at

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[12] Ibid; p. 208.

[13] Ibid; p. 208.

atmospheric pressure and equipped with an efficient fractionating column. The remainder of the solvent is removed by vacuum distillation at pressures of from 140 to 160 mm. of mercury.[14]

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[14]Naves, Y. R., and Mazuyer, G.; Natural Perfume Materials, Reinhold Publishing Corporation, New York, 99 (1947).

PINE NEEDLE OILS

Commercial production of pine needle oils is carried out in both Europe and Canada. No reference consulted indicated commercial production at the present time in the United States. In 1946, Russia exported 69,800 pounds of Siberian pine needle oil to this country. This was an increase of 5,750 pounds over 1945 shipments. Canada's exports of pine needle oil to the United States increased from 3,300 pounds in 1945 to 23,600 pounds in 1946.[15]

Steam distillation of pine needles yields varying percentages of oils from different species of pines. It also yields different percentages from the same species at different seasons of the year. Table I gives percentage values reported in the literature. Sandermann steam

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TABLE I

PERCENTAGE NEEDLE OIL

Species	Percentage Oil	Reference*
Pinus Sylvestris	0.133 to 0.6	16
Pinus Sylvestris	0.22 to 0.34	17
Pinus Sylvestris	0.12	18
Pinus Pumilio	0.25 to 0.75	16
Pseudotsuga Taxifolia (U. S.)	0.8 to 1	16
Pseudotsuga Taxifolia (Brit.)	0.01 to 0.11	16
Pseudotsuga Taxifolia (Brit.)	0.163	19

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[15]Schimmel and Company, Inc., Annual Report on Essential Oils, Aromatic Chemicals and Related Materials, New York, 51 (1946).

*See footnotes on page 10.

TABLE I, continued

Species	Percentage Oil	Reference
Pinus Sabiniana	0.078 to 0.102	16
Pinus Contorta	0.234	19
Pinus Ponderosa	0.04 to 0.126	16
Pinus Ponderosa	0.112	19
Pinus Lambertiana	0.045 to 0.120	16
Pinus Lambertiana	0.088	19
Pinus Palustris	0.401	19
Pinus Palustris	0.42	20
Pinus Heterophylla	0.271	19
Tusga Heterophylla	0.12	21
Pinus Contorta	0.234	19
Pinus Monticola	0.053	21
Pinus Insularis Endlicher	0.043	22
Juniperus Scopulorum	0.49	23
Abies Magnificia	0.14	19
Abies Concolor	0.128	19

distilled needles gathered from the Pinus Sylvestris in December, April, and June. He found that the December needles contained 0.22% oil, the April needles 0.25%, and the June needles 0.34%.[24] Parry reports 0.5%

[16] Parry; op. cit., pp. 53-60.

[17] Sandermann, Wilhelm; "Uber das schwedische Kiefernadelol und Bestandteile", Seifensieder-Zeitung, 66, 803 (1939).

[18] Chemical Abstracts; 25, 4727 (1931).

[19] "The Essences of Pine Needles", Perfumery and Essential Oil Record, 11, 97 (1920).

[20] Wahlenberg; op. cit., p. 24.

[21] Chemical Abstracts, 25, 4088 (1931).

[22] Ibid., p. 6002.

[23] Lehman and Lynn; op. cit., p. 1075

[24] Sandermann, op. cit., p. 803.

oil from June distillation and 0.133% from December distillation of needles from the Pinus Sylvestris.[25]

Very few references were available which gave information on needle oil from the Pinus Palustris. Parry reports the oil to have a specific gravity of 0.883 to 0.885, optical rotation of -26° to -31°, refractive index of 1.4810 to 1.4830, and esters as bornyl acetate of 1.5 to 2%. The constituents of the oil are furfural, l-pinene, l-camphene, dipentene, cadinene, and borneol and its esters.[26] Wahlenberg reports a specific gravity of 0.8829 to 0.8849 and principle constituents of camphene, b-pinene, cadinene, and borneol.[27]

No literature reference was found which indicated experimental work on the obtaining of pine needle oil by solvent extraction.

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[25] Parry, op. cit., p. 53.

[26] Ibid., p. 61

[27] Wahlenberg, op. cit., pp. 24, 25.

EQUIPMENT AND ACCESSORIES

Extraction equipment used consisted of four soxhlet extractors (figure 3) and one modified soxhlet extractor (figure 4). The soxhlet extractors had a capacity of approximately two hundred milliliters of pine needles. The solvent flask was of 300 ml. capacity and was connected to the extractor by a 24/40 ~~35~~ ground glass joint. The water-cooled reflux condenser fitted into the top of the extractor with a 55/50 ~~35~~ ground glass joint.

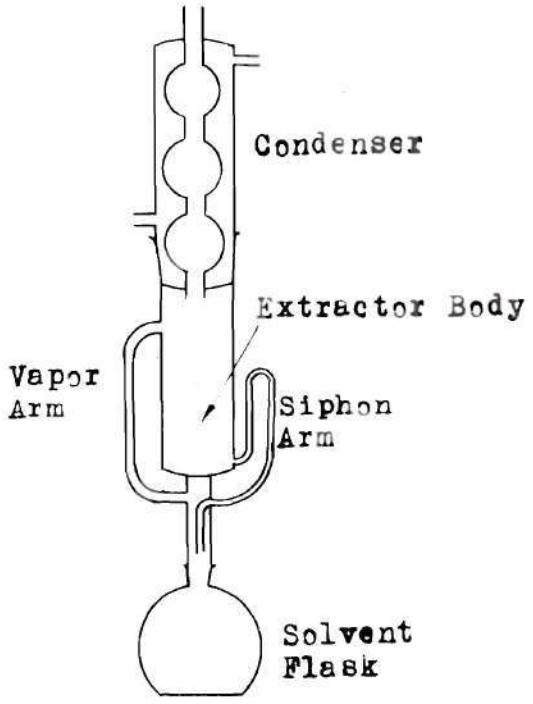

FIGURE 3: SOXHLET EXTRACTOR

The modified soxhlet extractor had a capacity of approximately 2.2 liters of pine needles. It was connected to a 3 liter solvent flask

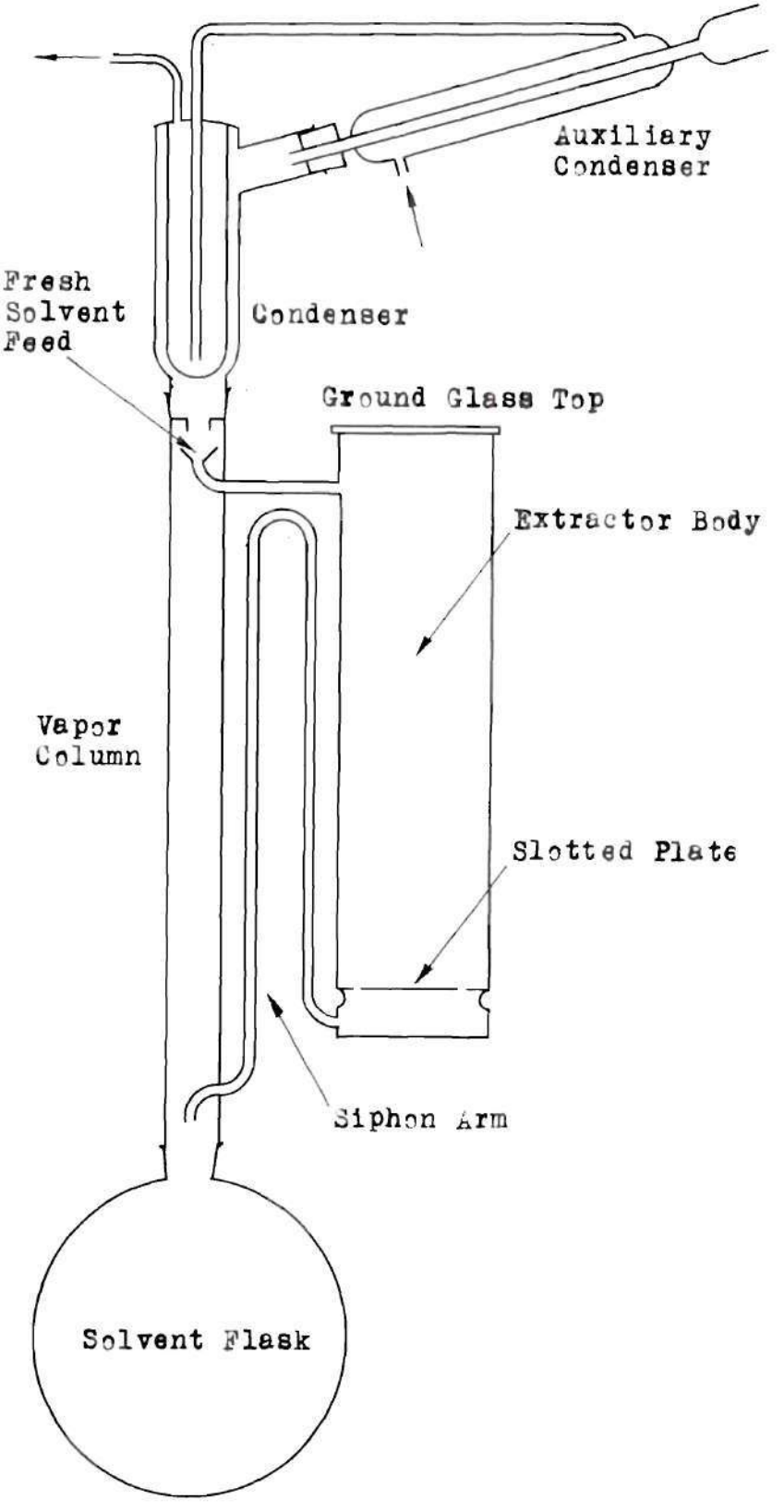

FIGURE 4: MODIFIED SOXHLET EXTRACTOR

by a 29/42 ⅋ ground glass joint. The water-cooled condenser fitted into the top of the vapor column with a 45/50 ⅋ ground glass joint. The top of the extractor body was closed with a ground glass plate which was held in place by two rubber bands. A slotted glass plate fitted near the bottom of the extractor body to support the material to be extracted and keep the siphon tube from being clogged with this material. When petroleum ether was used as the solvent in the modified soxhlet, it was necessary to add an auxiliary condenser connected in series with the main condenser by a cork stopper in order to recover the solvent vapor which would otherwise escape through the main condenser. Ice water was circulated through both condensers as the cooling medium by a Model B, Eastern Centrifugal Pump.

The solvent was removed from the extract by distillation at atmospheric pressure using a Vigreux column (figure 5) connected to a water-cooled condenser. The final residual amount of solvent was removed by distillation under vacuum produced by an aspirator.

Distillation of the extract itself was done under vacuum varying from 30 to 1/2 mm. of mercury using a 1 inch glass column 12 1/2 inches high with 7 3/4 inches of its height packed with 1/4 inch diameter raschig rings (figure 6). The packed portion of the column was lagged and heated in order that the high boiling constituents might be distilled. The portion of the column wall that was not lagged provided sufficient cooling for reflux. The column was connected to a distilling flask of 150 ml. capacity by a 24/40 ⅋ ground glass joint. Dow-Corning

silicone high vacuum stopcock grease was used and the connection was sealed with DeKhotinsky cement. Rubber connections in the system were coated with shellac to diminish leaks into the vacuum system. A Centigrade thermometer was inserted into the top of the column through a one-hole rubber stopper. The bulb of this thermometer reached just below the outlet vapor side arm of the column. All distillation temperatures mentioned hereafter were measured with this thermometer.

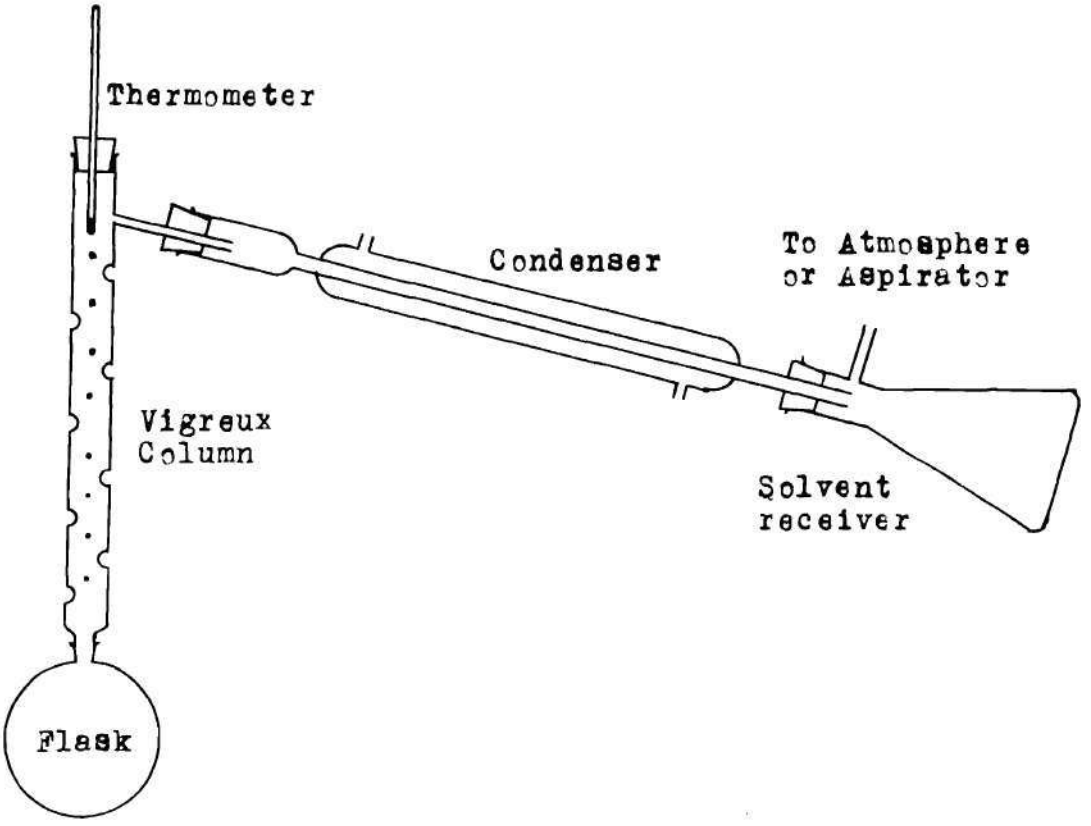

FIGURE 5: DISTILLATION SYSTEM FOR CONCENTRATING EXTRACT

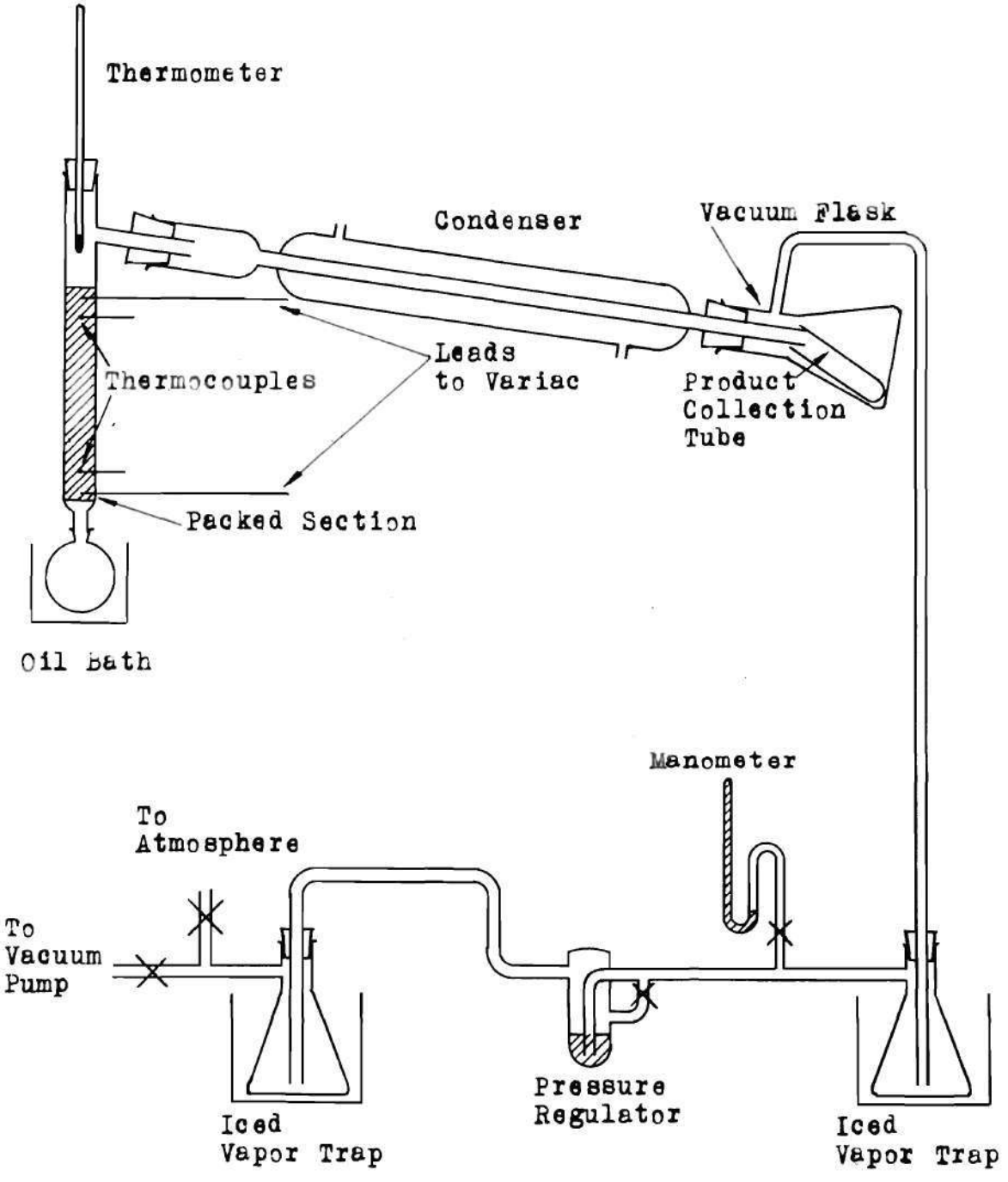

FIGURE 6: FRACTIONAL DISTILLATION SYSTEM

In order to prevent excessive condensation in the rectifying section, the column was heated by electrical resistance winding. B & S Number 20 nichrome wire was wound around 1/8 inch thick asbestos sheeting which surrounded the packed portion of the column. These windings were then covered by 1/4 inch asbestos sheeting. Heat input to the column was controlled by a Variac built by the Superior Electric Company. Column wiring was designed for a maximum input of 150 watts. Column wall temperature was measured by two iron-constantan thermocouples which were inserted, one near the top and one near the bottom of the column, between the asbestos and the glass column wall. Thermocouple readings were made using a Leeds and Northrop potentiometer. The vacuum was provided by a Cenco Pressovac pump operated by a 1/4 horsepower Emerson electric motor. The vacuum system included two cold traps, a manometer, and a pressure regulator.

EXPERIMENTAL PROCEDURE AND RESULTS

Soxhlet extractors were used to obtain rate data for 5 different solvents; acetone, petroleum ether (boiling range 35-60° C), benzene, isopropyl alcohol, and methyl ethyl ketone. A simultaneous check run was made with each solvent. A check run using acetone in one extractor and benzene in the other was also made.

Needles used in all extractions were gathered in September of 1949 from young long-leaf pine trees (of Pinus Palustris) near Valdosta in Lowndes County, Georgia. The height of the trees from which the needles were gathered varied from five to twenty feet. The needles were allowed to dry at room temperature before extractions were made.

The extraction procedure followed was to fill the extractor with pine needles which had been previously cut in approximately one inch lengths, weighed, and crushed by pounding in a mortar. The amount and degree of crushing was maintained the same from sample to sample as nearly as possible. Preliminary extractions were carried out without crushing the needles, but extraction rates were too low to be of practical value. Also any commercial operations would include preliminary crushing. 210 ml. of solvent were poured into the solvent flask, the extractor was assembled, and extraction was commenced by boiling the solvent using either a water or oil bath over a bunsen flame. Extraction time was counted from the time that the first reflux began dripping over the needles. When the extractor was completely filled, the siphon action flushed the solvent and extract back into the solvent flask. The

time of each siphon cycle was recorded. The first analysis of percent extract was made at the end of either one or two siphon cycles.

Just before analysis, the extractor was allowed to almost fill before the solvent flask was removed from the extractor. This served to remove the larger part of the solvent from the extract while the material was still in the extractor. The solvent flask was then disconnected from the extractor and the solvent and extract were filtered into a weighed flask. The solvent flask was rinsed several times with fresh solvent and the washings were poured through the filter paper into the weighed flask. About 50 ml. of solvent was then added to the solvent flask and extraction was renewed.

The weighed flask and its contents of solvent and extract were then connected to a Vigreux column, and the solvent was driven off by heating in a water bath. Last traces of solvent were removed under vacuum produced by an aspirator. The flask and extract were allowed to cool and then weighed. Difference in the weight of flask plus extract and the weight of the empty flask gave the weight of the extract. This was divided by the weight of pine needles started with and multiplied by one hundred to give the percentage weight of material extracted from the needles. Five or six points were obtained in this way for each batch of pine needles extracted. The percentages obtained for each solvent tested were plotted both as a function of extraction time and as a function of the number of times the extractor filled with solvent (extraction cycles). Figures 7 through 16 give the plots obtained.

The results show that the greater part of the extractable material was removed during the first few cycles of solvent through the extractor. Even after the first cycle, the extraction rate began to fall off sharply. The check in percentage of extract obtained in the two runs with each solvent was in general as good or better than was expected when one considers the fact that pine needles are a product of nature and did not all come from the same tree.

The different solvents removed varying percentages of extractable (soluble) material from the needles. The largest percentage was obtained using isopropyl alcohol. The yield was 9.1% extract (% of pine needles) for run 13 and 9.03% for 14. However, the product in the last few analyses was hard and crusty. This indicated either that high molecular weight material was being extracted or that a chemical reaction between solvent and extract was taking place. Extraction with petroleum ether gave the smallest percent yields. Run 9 gave a yield of 3.41% and 10 gave 3.22%. Extraction with acetone gave good yields, and this solvent was the easiest to handle both during extraction and in the removal of the solvent from the extract. Table II shows the average percent of extract obtained using the various solvents at the end of ten hours extraction.

Extraction rate experimental data are tabulated in Tables III through VII. These data are presented in graphical form in figures 7 through 16.

Figure 7 is a plot of extract in percent pine needle weight versus time in minutes using acetone as the solvent. Runs 7 and 8

gave curves of approximately the same shape and percent extract. The percent extract obtained for run 17 was considerably lower than that obtained for runs 7 and 8. Run 17 gave a percentage yield of only 7.13,

TABLE II

AVERAGE PERCENT EXTRACT WITH DIFFERENT SOLVENTS

Solvent	Average Percent Extract
Acetone	8.08
Petroleum Ether	3.20
Benzene	5.47
Isopropyl Alcohol	8.81
Methyl Ethyl Ketone	7.05

while runs 7 and 8 gave a percentage yield of 8.59 and 8.50 respectively. Run 17 was made a considerable time after runs 7 and 8 and pine needles from a different group of trees were used. In all three curves, over 50% of the total extracted product was obtained during the first thirty minutes of extraction time, and over 85% was obtained during the first two hundred minutes. Extractions with acetone were more than 550 minutes. However, the needles were not completely exhausted of extractable material at that time; nor were they completely exhausted in runs made with any of the other solvents.

Figure 8 is a plot of extract in percent pine needle weight versus time with petroleum ether used as the solvent. The curves of

runs 9 and 10 are found in this figure. The shape of the curves is the same as that of run 17 with acetone as solvent. However, the percentage product extracted was much smaller. At the end of over 900 minutes extraction time, run 9 produced only 3.41% extract and run 10 produced 3.22%. Well over 50% of total extracted material was obtained in the first thirty minutes of extraction time and over 85% in the first two hundred minutes. Petroleum ether dissolved less of the green coloring material in the needles than any other solvent tested. The needles had a distinct green color after more than nine hundred minutes of extraction.

Figure 9 shows the relationship between time and percent extract with benzene as the solvent. The curves here had the same general form as those already discussed. Again, over 50% of the total material extracted was obtained during the first thirty minutes of extraction. At the end of 200 minutes, over 95% of total material extracted had been removed. Runs 11 and 12 were made at the same time and yielded 5.95% and 5.31% extract respectively. Run 18 was a check run made at a later date, and it gave a yield of 5.26% extract.

Figure 10 gives the results obtained from runs 13 and 14. These runs were made using isopropyl alcohol as the solvent. Agreement between the two curves was very close. In total percentage, run 13 yielded 9.10% extract in percent pine needle weight and run 14 yielded 9.03%. Again, more than half of the total material extracted was obtained during the first thirty minutes. Slightly over 80% was obtained

during the first two hundred minutes. The curves obtained with isopropyl alcohol as the solvent were of the same shape as those obtained using the other solvents, but the slope was steeper during the latter part of the extraction than was the case with the others. The last extracts obtained with isopropyl alcohol were hard and crusty, whereas those obtained with the other solvents used were tarry.

Results of runs 15 and 16 are presented in figure 11. These runs were made with methyl ethyl ketone as the solvent. The results obtained are quite similar to those from run 17 made with acetone. Run 15 yielded a total of 6.94% extract in percent pine needle weight and run 16 yielded 7.63%. Over 85% of the total extract was obtained by the end of 200 minutes.

Figures 12 through 16 present the same percentages of extract as figures 7 through 11, but they are plotted as a function of extraction cycles. The curves contain one point less than do those plotted against time, as extraction cycles were not counted for the last sample taken in each run. The time per extraction cycle did not vary sufficiently to make these curves differ appreciably from those plotted against time, therefore the curves will not be discussed individually. In every case, over 50% of the total material extracted was obtained by the end of the second extraction cycle.

The percent extract (% weight of pine needles) obtained with the various solvents at the end of 600 minutes was used as a base to divide into the percents of extract obtained at time periods less than 600 minutes. The resulting fraction was multiplied by 100 to give the

percent of total product extracted based on the extract at the end of 600 minutes being considered as 100%. The average percents of extract based on the weight of pine needles extracted were obtained from the curves in figures 7 through 11. These data as well as those calculated as described above are presented in Table VIII.

The percentages of total extract (based on 100% at 600 minutes) were plotted as a function of time on logarithmic graph paper (figure 17). The resulting plot is a straight line correlation of data from all solvents used. The average deviation of the plotted points from the line drawn through them is ±3.74%. The maximum deviation is 13%. Rate data from extractions with benzene did not fit the correlation so well as data from extractions with the other solvents.

A similar correlation (figure 18) was made using extraction cycles rather than time as the abscissa of the plot. The plot was based on the extract at the end of 25 cycles being considered as 100%. Data for this correlation are given in Table IX. The average deviation of the points from the curve drawn through them is ±3.04%. The maximum deviation is 13%.

The modified soxhlet extractor was used to obtain enough extract so that a fractional distillation of the extract could be made under vacuum. The needles used in this extractor were pulverized in a hammer mill, weighed, and charged into the extractor. Approximately 350 grams of needles and 2.7 liters of solvent were used in each extraction. Three extractions were made using acetone as the solvent and five were made using petroleum ether. Removal of solvent from extract was

accomplished in the same manner as in the case of the material extracted with the small soxhlets. The overall percentage yield with acetone as the solvent was 8.91%. With petroleum ether as the solvent, the overall yield was 4.04%. The specific gravity of the extract obtained with acetone was 1.061 $30^{\circ}/15^{\circ}$. That for the extract obtained with petroleum ether was 0.934 $30^{\circ}/15^{\circ}$. It was necessary to measure the sp. gr. of the extracts at the higher temperature of 30°C because of their semisolid state at lower temperatures. Both extracts were olive green in thin layers and appeared almost black in thicker quantities. Both were very viscous at room temperature. The extract obtained with acetone was darker and more viscous than that obtained with petroleum ether. The refractive index of the extract obtained using petroleum ether was $n_d^{20^{\circ}}$ 1.510. The very fuzzy dividing line obtained with the refractometer prevented a more accurate reading. No refractive index was found for the acetone extract. This extract was very thick and was not completely homogeneous.

Both extracts were distilled under vacuum in an attempt to separate the lower boiling oils which are normally obtained by steam distillation. Weighed quantities of extract were distilled starting at pressures as high as 30 mm. of mercury and finally reaching a pressure of 1/2 mm. Both oil bath and column wall temperatures were gradually raised as the distillation progressed. Tables X and XI give the results of the fractional distillation. Distillates were collected in weighed tubes, and the weights of the distillates were then determined from the difference in the weight of tube plus distillate and

the weight of the empty tube. Quantities of the distillates were so small that the only test made on them was the refractive index. Figures 19 and 20 show plots of boiling point at 1/2 mm. pressure versus percent overhead and of refractive index versus percent overhead.

Where actual pressures varied from 1/2 mm., it was necessary to correct the observed boiling point to the boiling point at 1/2 mm. This value was obtained from an extrapolation of a Cox chart[28] (extrapolation was made from 1 mm. to 1/2 mm. pressure). Vapor pressure data[29] of alpha-pinene, menthone, and borneol were plotted on the Cox chart in order to show that the terpines fit roughly into the same family as the saturated aliphatic hydrocarbons given in the chart. In making an estimation, a point corresponding to the observed boiling point at the observed pressure was located on the chart. A straight line fitting into the family of existing lines was drawn to the 1/2 mm. pressure line, and the temperature was read at the point where these two lines intersected.

Distillation of the extract obtained with acetone was commenced at too low a pressure (10 mm.) and condensation took place in the iced vapor trap instead of in the condenser. The temperature of the oil distilling over was not high enough to cause the mercury to rise above the top of the rubber stopper in the top of the distilling column, so it

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[28]Hougen, O. A., and Watson, K. M., Chemical Process Principles, Part I, John Wiley & Sons, New York, 66 (1943).

[29]Guenther, op. cit., pp. 389, 398.

was not known at what temperature distillation took place for the first two samples. The first sample was collected by pouring it from the vapor trap into the collection tube. It contained two liquid phases. The larger, bottom phase gave a refractive index of $n_d^{20^\circ}$ 1.3731. Not enough of the other phase was present to permit a refractive index of it to be measured.

When distillation temperatures reached 80° C, condensation occurred in the side arm of the fractionating column; and condensate collected in the neck of the condenser. In two instances noted in Table X, a very small amount of product condensed in the condenser while the main product condensed in the side arm and collected in the neck of the condenser. These small products condensing in the condenser were omitted in the plot of refractive index versus percent overhead because they had a much lower refractive index than the main product and appeared to be products of decomposition. Near the end of the fractionation there was evidence of a considerable amount of decomposition.

Better results were obtained in the distillation of extract obtained with petroleum ether. Distillation was commenced at 25 mm. of mercury and the cooling water for the condenser was refrigerated. The pressure was subsequently reduced to 1/2 mm. as distillation temperature rose. There was distinct evidence of pyrolysis while the last sample was being distilled.

Refractive indices for the first two samples collected from the distillation of the extract obtained using petroleum ether were in the

same range as refractive indices reported in the literature for pine needle oils. Refractive indices for other samples ran considerably higher. This indicates that higher boiling oils were obtained in the vacuum distillation than can possibly be obtained by steam distillation in a reasonable length of time. Quantities of oil obtained were too small to permit fractionation into individual compounds. However, fractions ranging from thin colorless oils to thick amber masses were obtained. Tables X and XI give the experimental data of the vacuum distillations including the weight andappearance of the samples collected. After the first distillation in the case of the petroleum ether extract and after the first two distillations in the case of the acetone extract, it was necessary to keep both oil bath and column wall temperatures relatively high in comparison with distillation temperatures in order to obtain any distillate. This means that the walls of the column in the packed section were superheating the vapor to some extent in order to overcome heat losses in the reflux section (unheated section of column). There was definite evidence of decomposition in the collection of the last sample of each distillation and some evidence of decomposition as early as sample three in the case of the distillation of extract obtained with acetone.

Table XII gives the data which were used in plotting figure 19. This figure is a plot of boiling point of the distillates from the acetone extracted sample corrected to 1/2 mm. pressure and of the refractive indices of the distillates versus the cumulative percent overhead. The indices plotted are those for the individual samples,

and they are plotted at the point of cumulative overhead represented by that sample. For example, sample number 5 represents only 10.9% of the total overhead, but when added with the percents of samples 1 through 4 it is 36.4% of the cumulative overhead. The refractive index of the successive samples rose rapidly until the overhead accumulated reached approximately 20%. After that point all readings were between 1.5019 and 1.5088. In general, the boiling point at the beginning of the distillation of one sample was lower than the boiling point at the end of the previous sample. This was caused by the necessity of bringing the system to atmospheric pressure in order to remove a sample and then reevacuating for the distillation of the next sample. It is assumed that a very small amount of lower boiling vapors present in the top of the column above the side arm condensed during this operation and were the first to distill when collection of the next sample was started.

Figure 20 was plotted from data presented in Table XIII. This figure is exactly the same type of plot as Figure 19. It is made for the distillates from the petroleum ether extracted sample. The curves follow the same trend as those of Figure 19, but smaller amounts of low boiling materials were collected. Initial refractive indices were considerably higher than those for the first two samples from the extract obtained with acetone as the solvent, and the indices for the last two samples were somewhat higher. In the range of from twenty to forty cumulative percent overhead the indices of the two fractionations were fairly close together.

CONCLUSIONS

From the results obtained in this investigation, the following conclusions can be drawn.

(1) A maximum of about 9% by weight of Georgia long-leaf pine needles is recoverable by solvent extraction.

(2) Over 70% of the material in the crushed pine needles which is extractable by any given solvent is removed after five washings with the hot solvents, and further extraction accomplishes but little.

(3) The amount of extract varies with the solvent and more than a two-fold difference in the amount of extract with different solvents was obtained.

(4) Percents of total amount of extract obtained plotted on logarithmic graph paper both as a function of time and as a function of extraction cycles give a straight line correlation applicable to all solvents tested.

(5) The solvent extracting the most material was found to be isopropyl alcohol, and the one extracting the least was petroleum ether.

(6) Oil having the same refractive index as commercial pine needle oil can be obtained from the extract by vacuum fractional distillation.

(7) Solvent extraction recovers a great deal more oil than does steam distillation.

(8) Oils of molecular weight too high for recovery by steam distillation may be obtained by solvent extraction.

(9) Further work on Georgia pine needles should be pointed toward isolation and identification of the individual constituents or groups in the extract and will require larger samples for vacuum distillation and larger extraction equipment.

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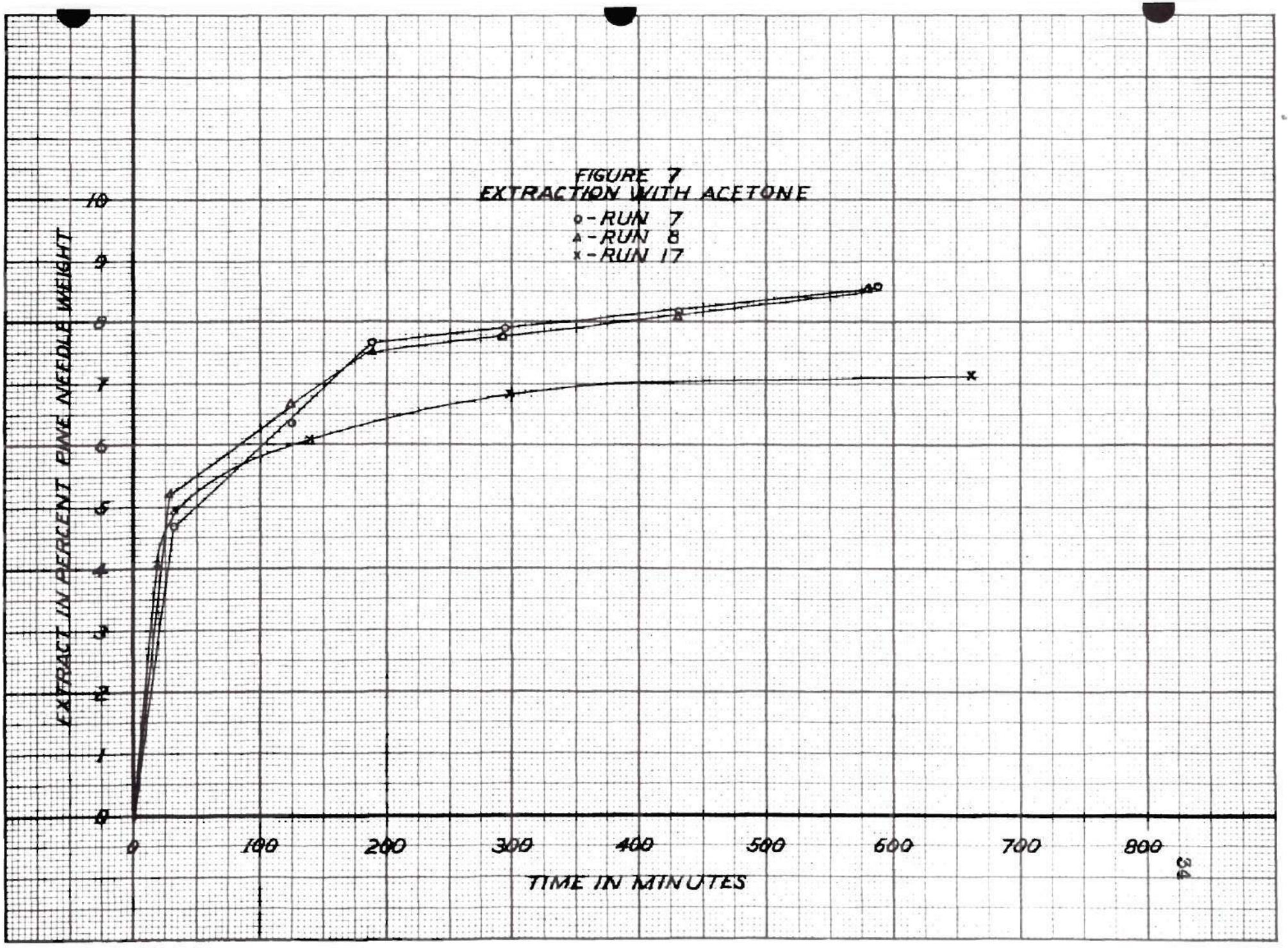
APPENDIX I

CURVES



FORM 5000
THE GEORGIA TECH COLLEGE INN

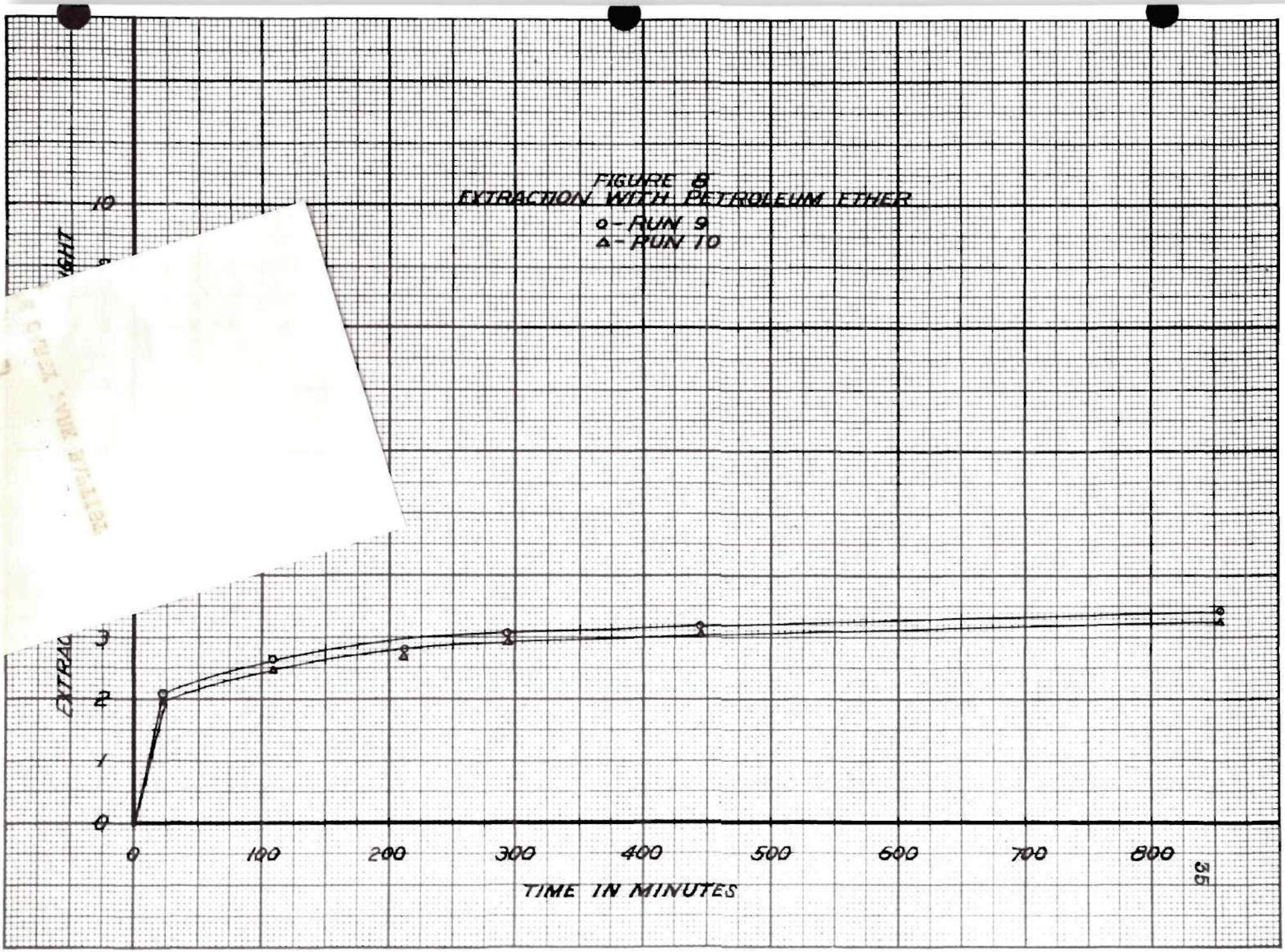


FIGURE 8
EXTRACTION WITH PETROLEUM ETHER
o - RUN 9
Δ - RUN 10
10
EXTRAC
3
2
1
0
0
100
200
300
400
500
600
700
800
TIME IN MINUTES

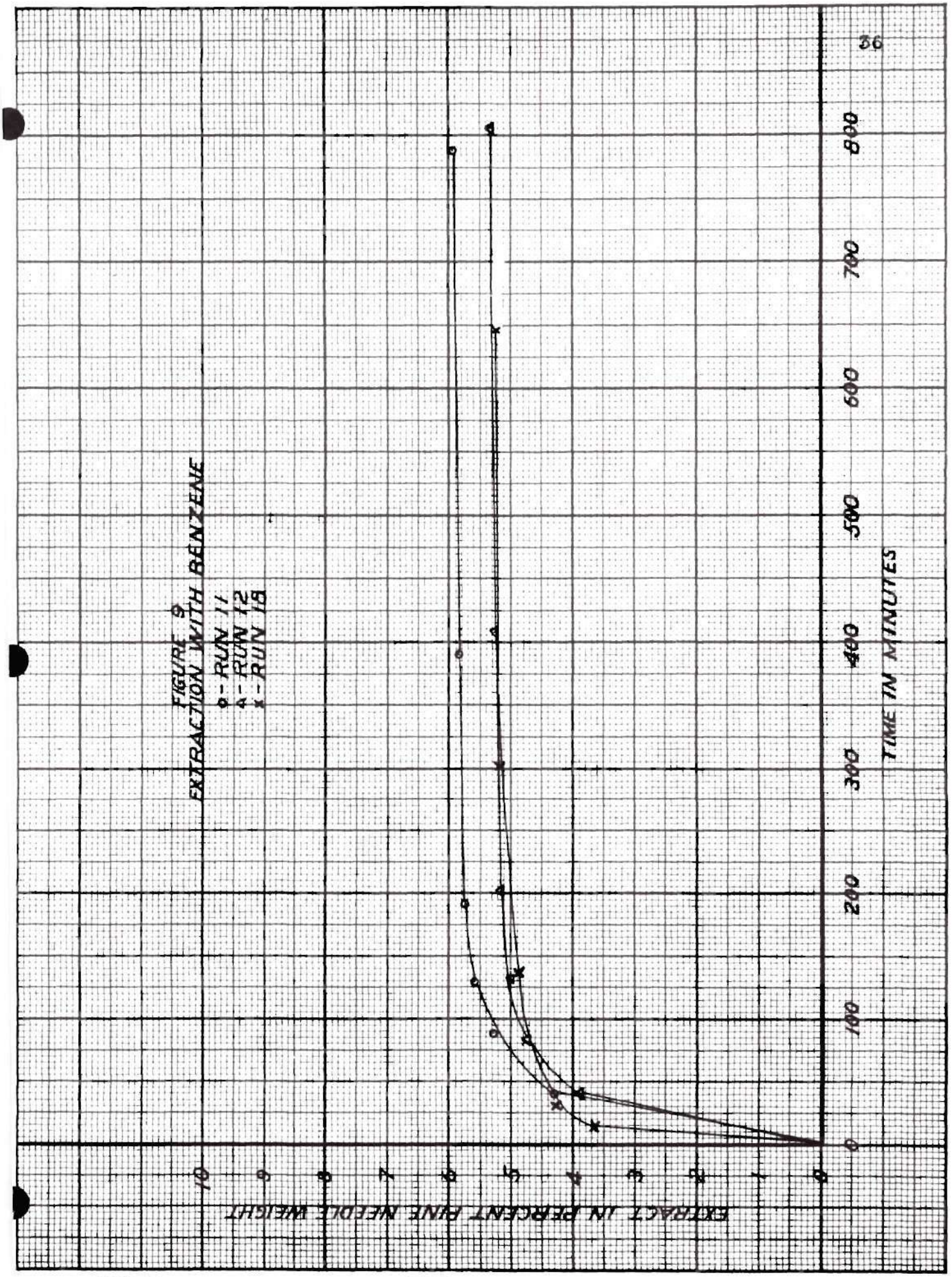
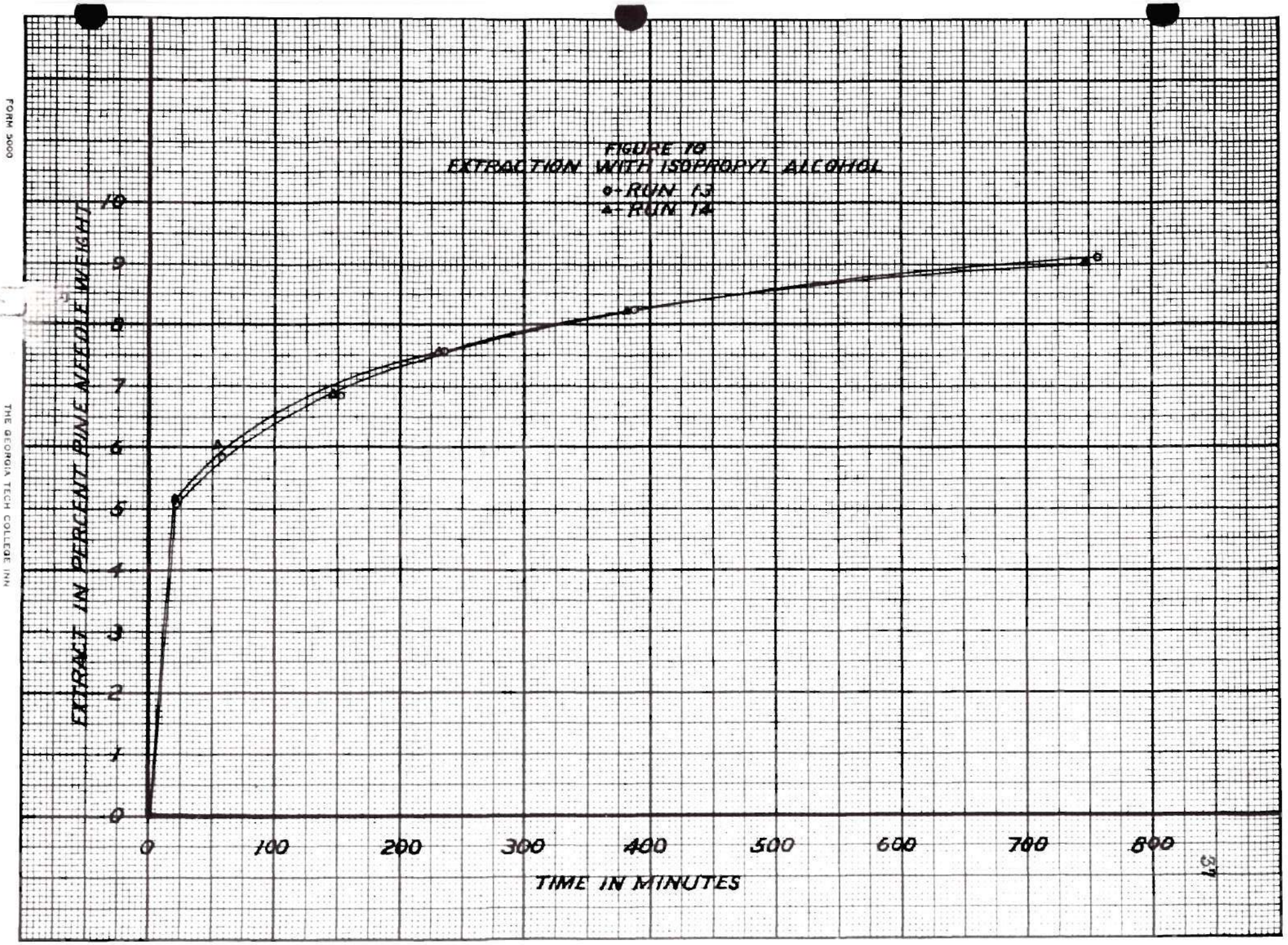


FIGURE 9
EXTRACTION WITH BENZENE
o - RUN 11
Δ - RUN 12
x - RUN 13
EXTRACT IN PERCENT PINE NEEDLE WEIGHT
TIME IN MINUTES
0
100
200
300
400
500
600
700
800
1
2
3
4
5
6
7
8
9
10



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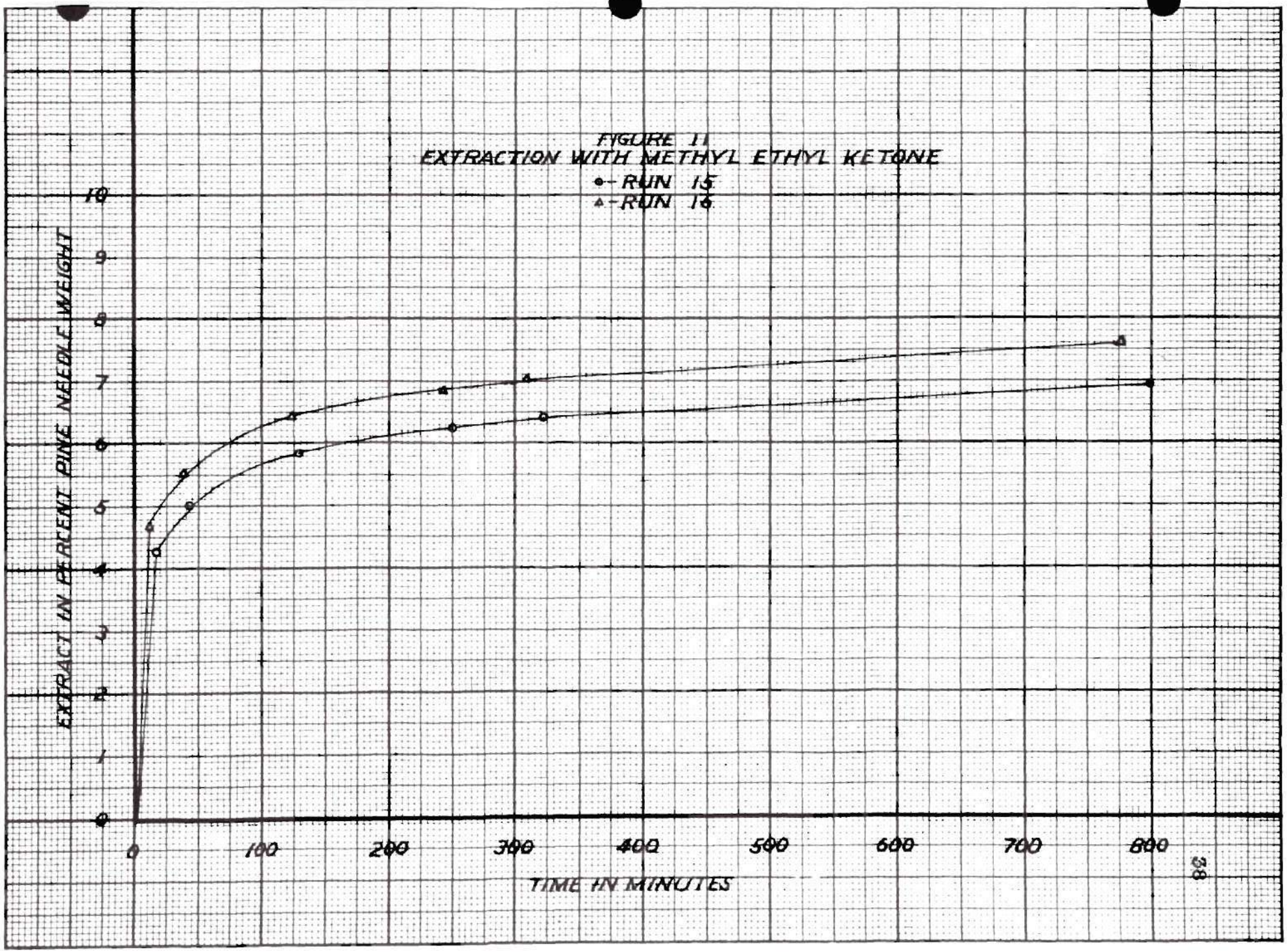
THE GEORGIA TECH COLLEGE INN



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THE GEORGIA TECH COLLEGE INN

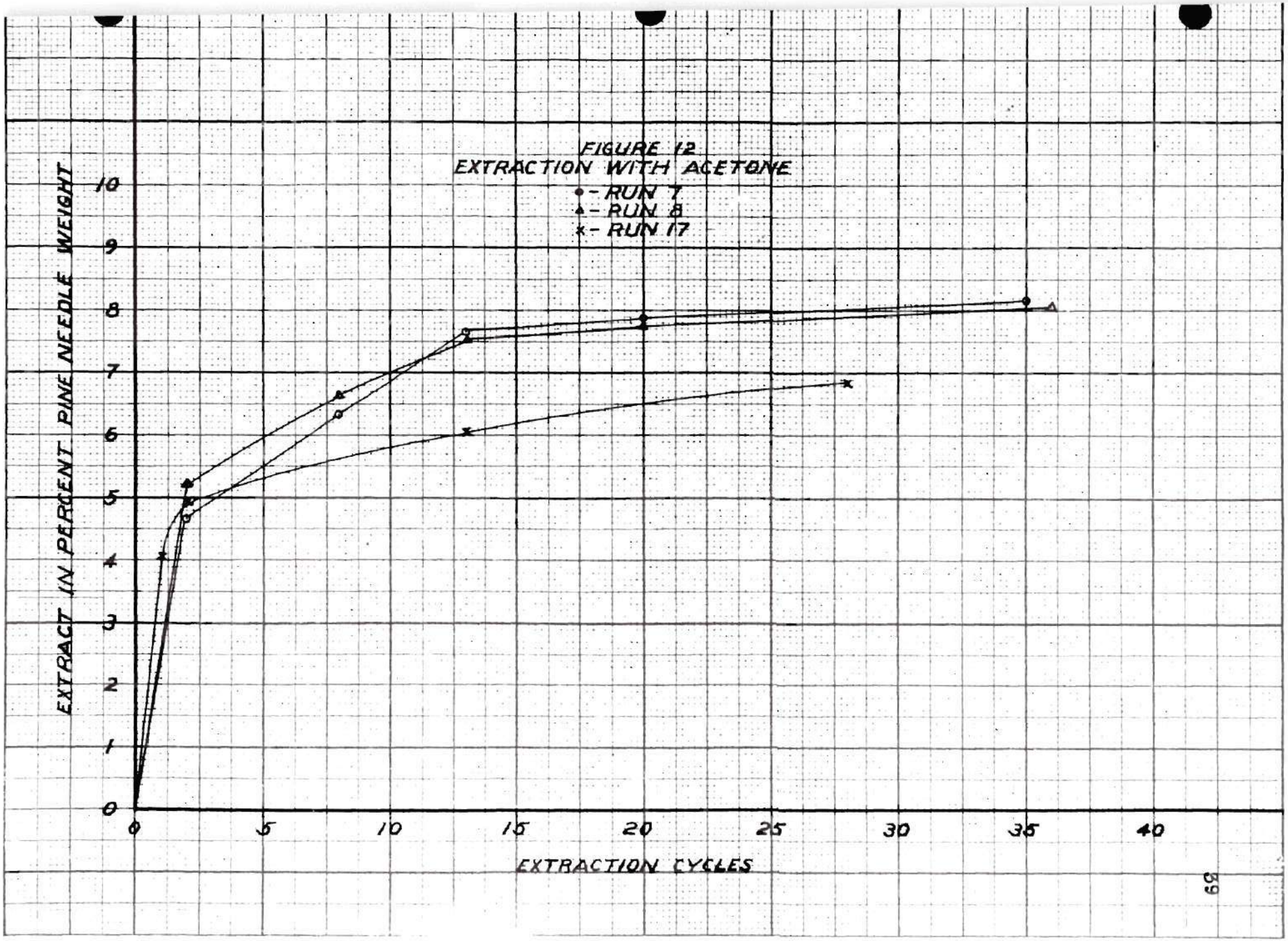
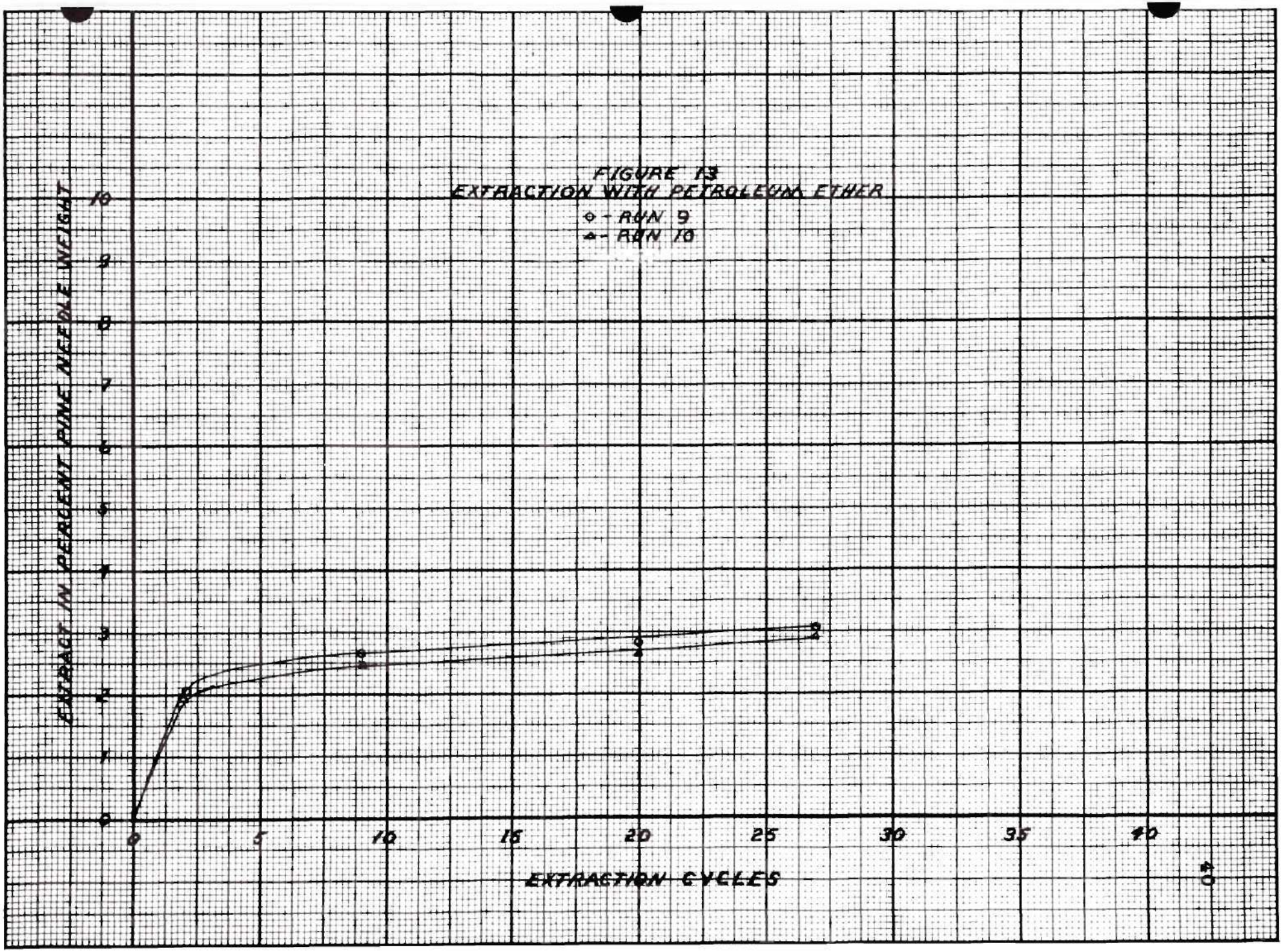


FIGURE 12
EXTRACTION WITH ACETONE
● - RUN 7
▲ - RUN 8
× - RUN 17
EXTRACT IN PERCENT PINE NEEDLE WEIGHT
0
1
2
3
4
5
6
7
8
9
10
0
5
10
15
20
25
30
35
40
EXTRACTION CYCLES

FORM 5000

THE GEORGIA TECH COLLEGE INN

FIGURE 13
EXTRACTION WITH PETROLEUM ETHER
◇ - RUN 9
△ - RUN 10



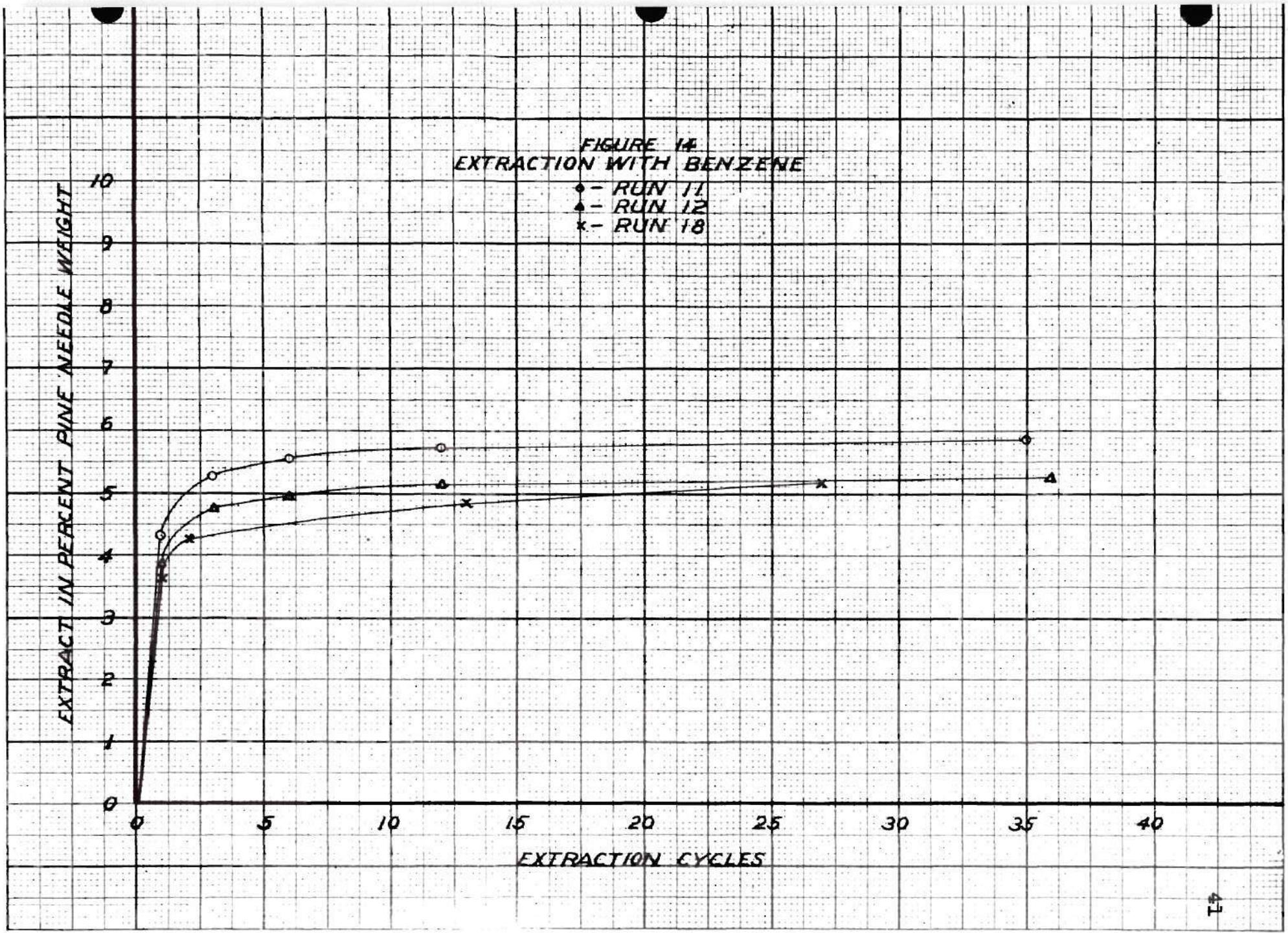


FIGURE 14
EXTRACTION WITH BENZENE
◆ – RUN 11
▲ – RUN 12
× – RUN 18
EXTRACT IN PERCENT PINE NEEDLE WEIGHT
0
1
2
3
4
5
6
7
8
9
10
0
5
10
15
20
25
30
35
40
EXTRACTION CYCLES

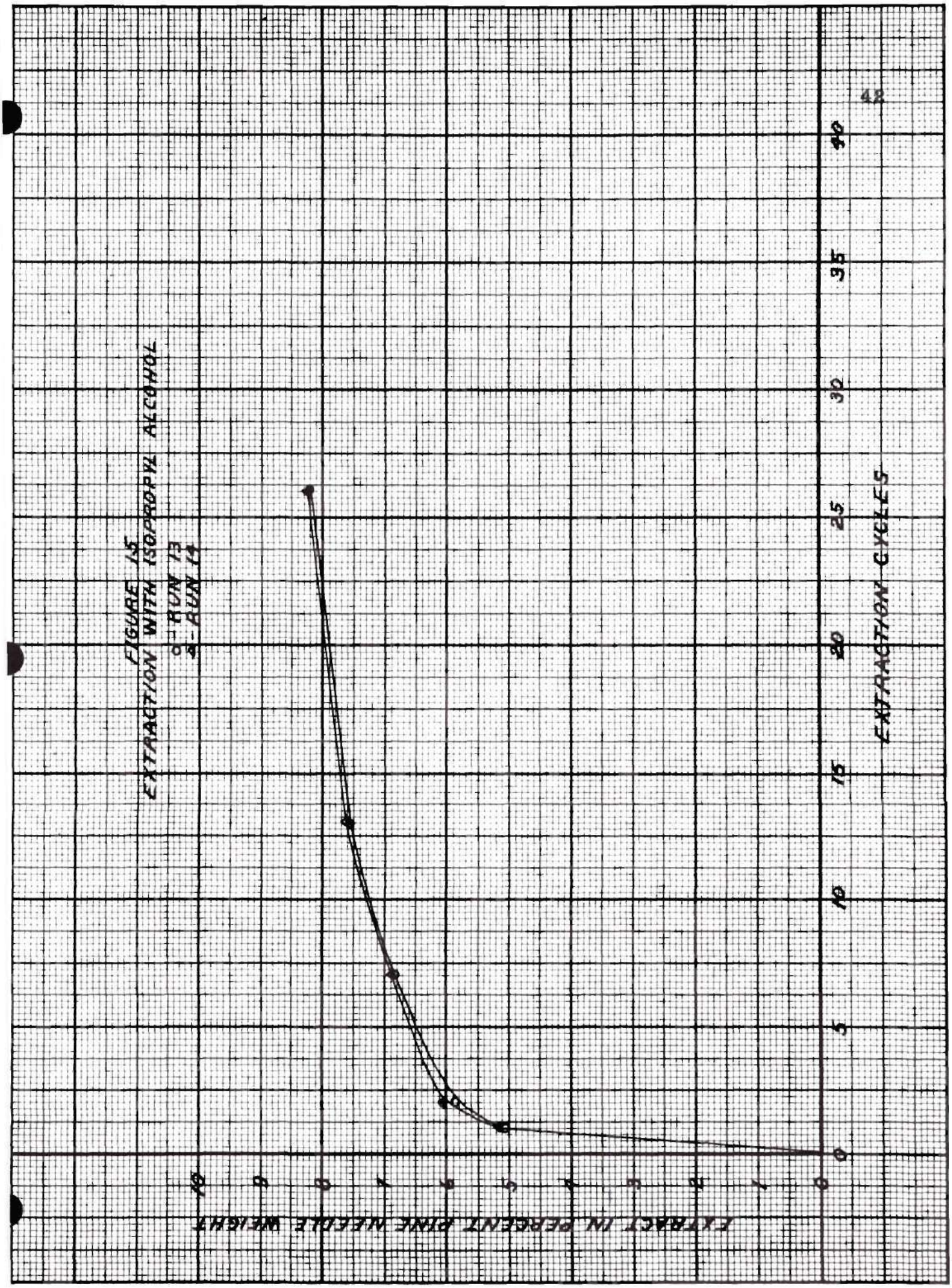
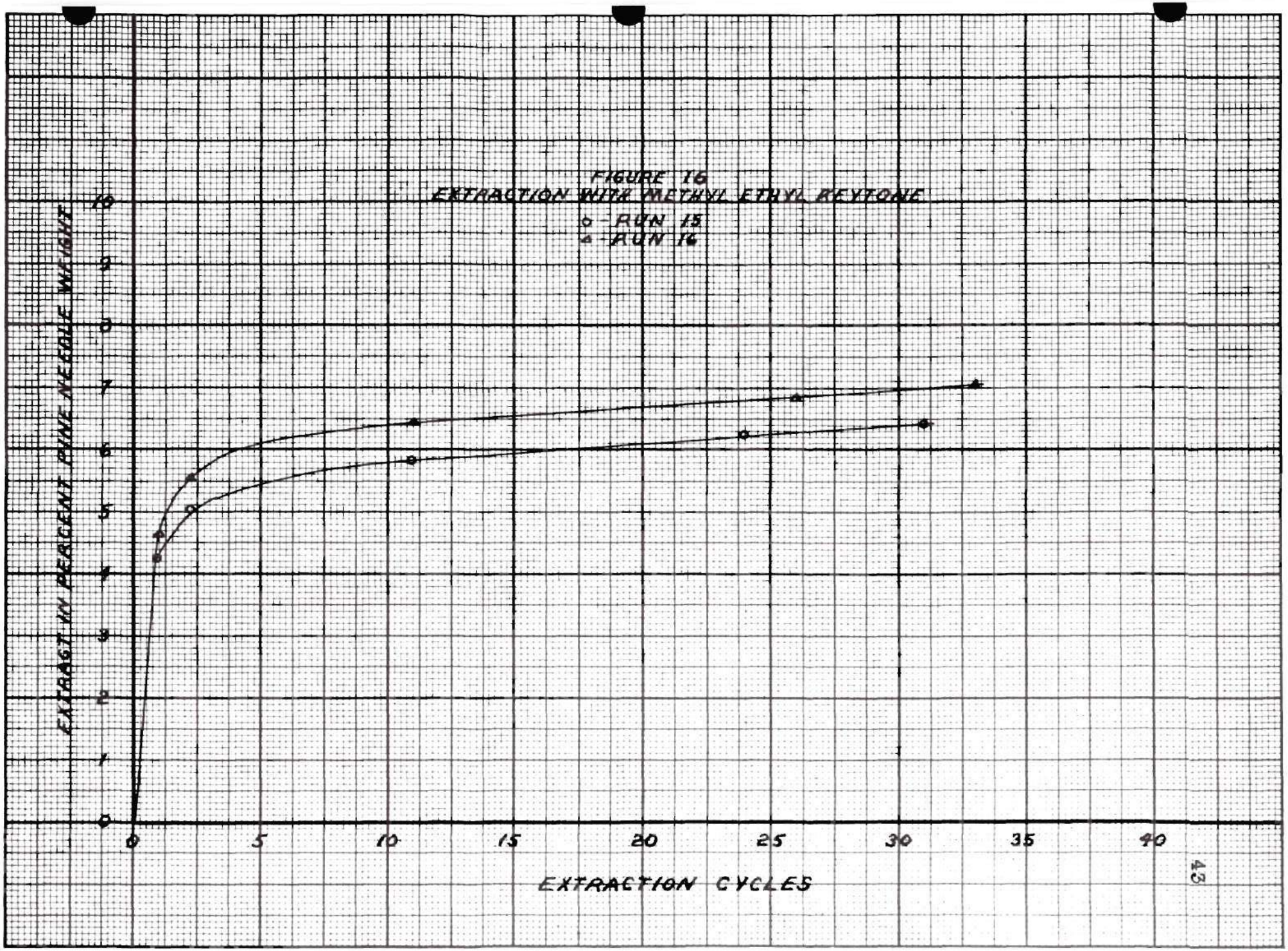


FIGURE 15
EXTRACTION WITH ISOPROPYL ALCOHOL
○ - RUN 13
● - RUN 14
EXTRACT IN PERCENT PINE NEEDLE WEIGHT
EXTRACTION CYCLES
0
5
10
15
20
25
30
35
40

FORM 5000

THE GEORGIA TECH COLLEGE INN

FIGURE 16
EXTRACTION WITH METHYL ETHYL KEYTONE
○ - RUN 15
△ - RUN 16



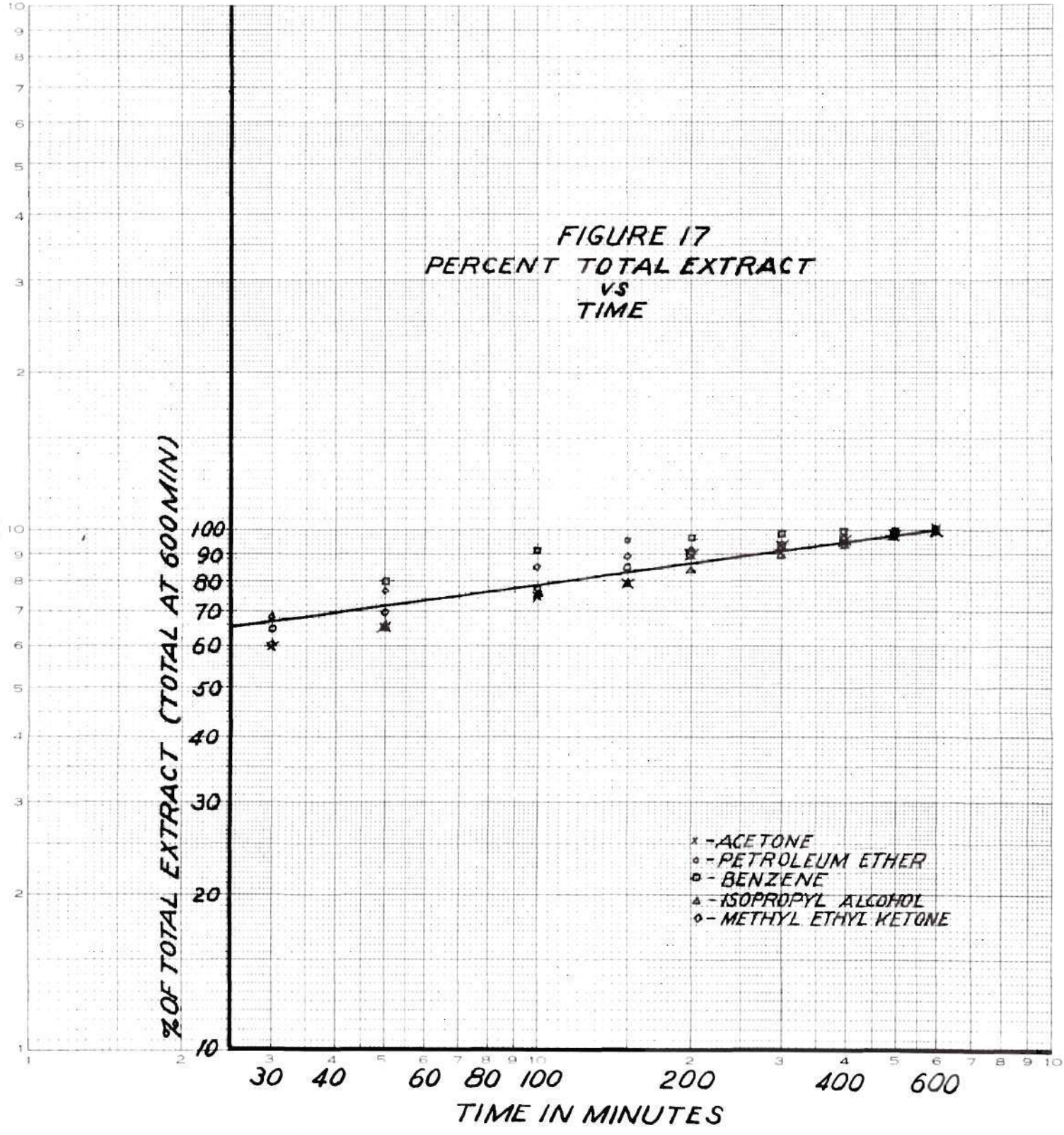


FIGURE 17
PERCENT TOTAL EXTRACT
VS
TIME
% OF TOTAL EXTRACT (TOTAL AT 600 MIN.)
100
90
80
70
60
50
40
30
20
10
30 40 60 80 100 200 400 600
TIME IN MINUTES
x - ACETONE
o - PETROLEUM ETHER
□ - BENZENE
△ - ISOPROPYL ALCOHOL
◇ - METHYL ETHYL KETONE

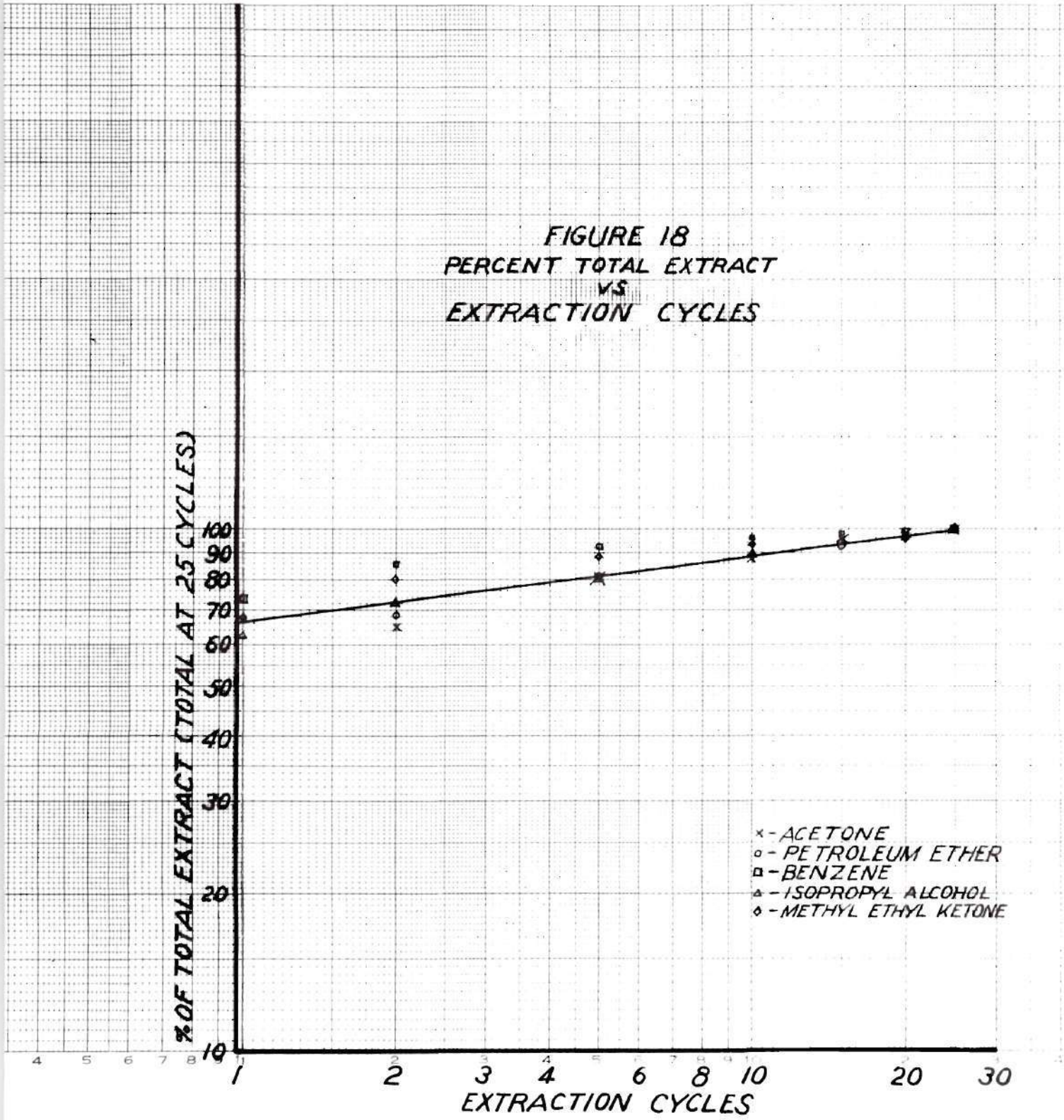


FIGURE 18
PERCENT TOTAL EXTRACT
VS
EXTRACTION CYCLES
% OF TOTAL EXTRACT (TOTAL AT 25 CYCLES)
100
90
80
70
60
50
40
30
20
10
1
2
3
4
6
8
10
20
30
EXTRACTION CYCLES
× - ACETONE
○ - PETROLEUM ETHER
□ - BENZENE
△ - ISOPROPYL ALCOHOL
◇ - METHYL ETHYL KETONE

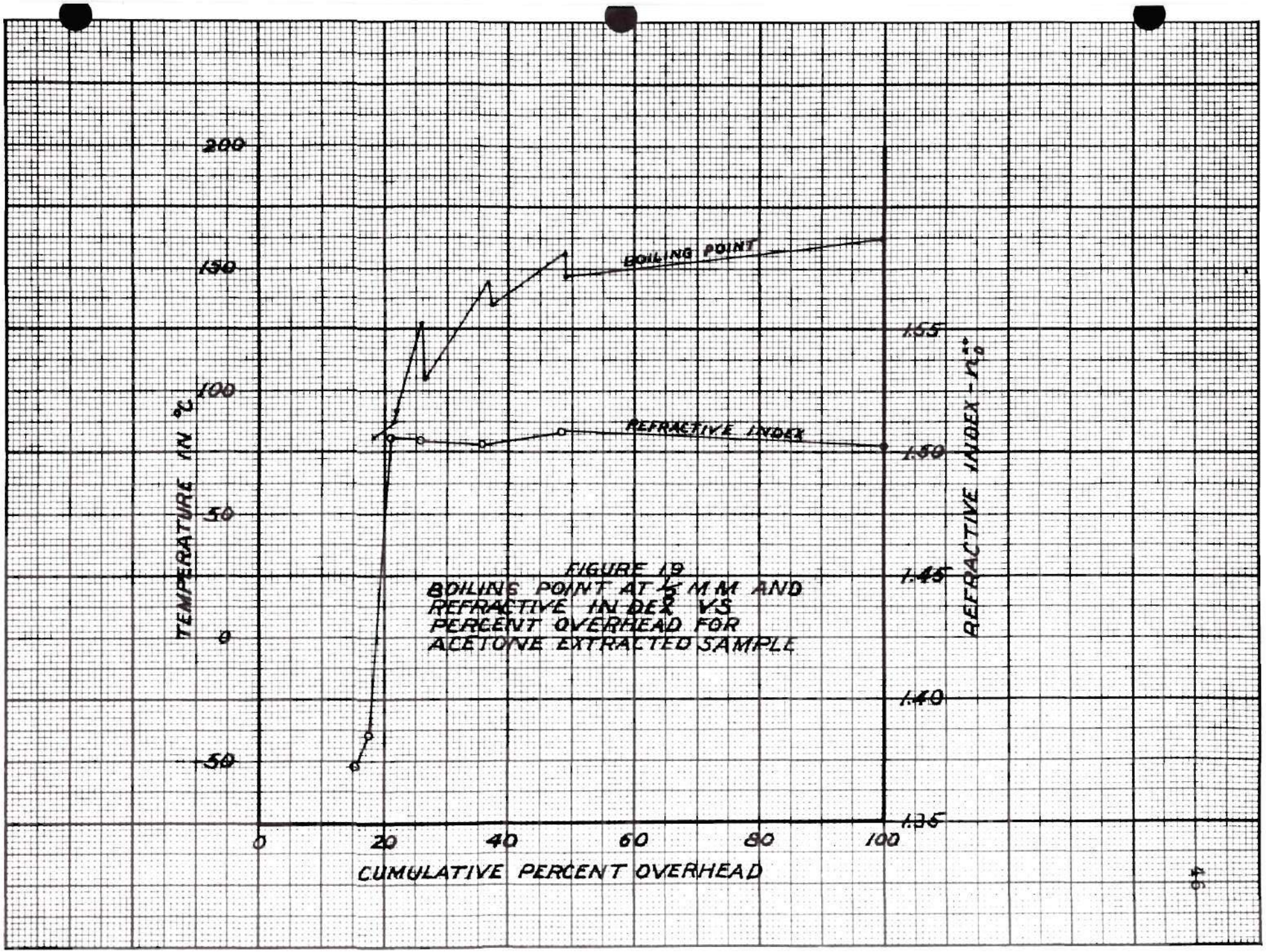


FIGURE 19
BOILING POINT AT 1/5 MM AND REFRACTIVE INDEX VS. PERCENT OVERHEAD FOR ACETONE EXTRACTED SAMPLE

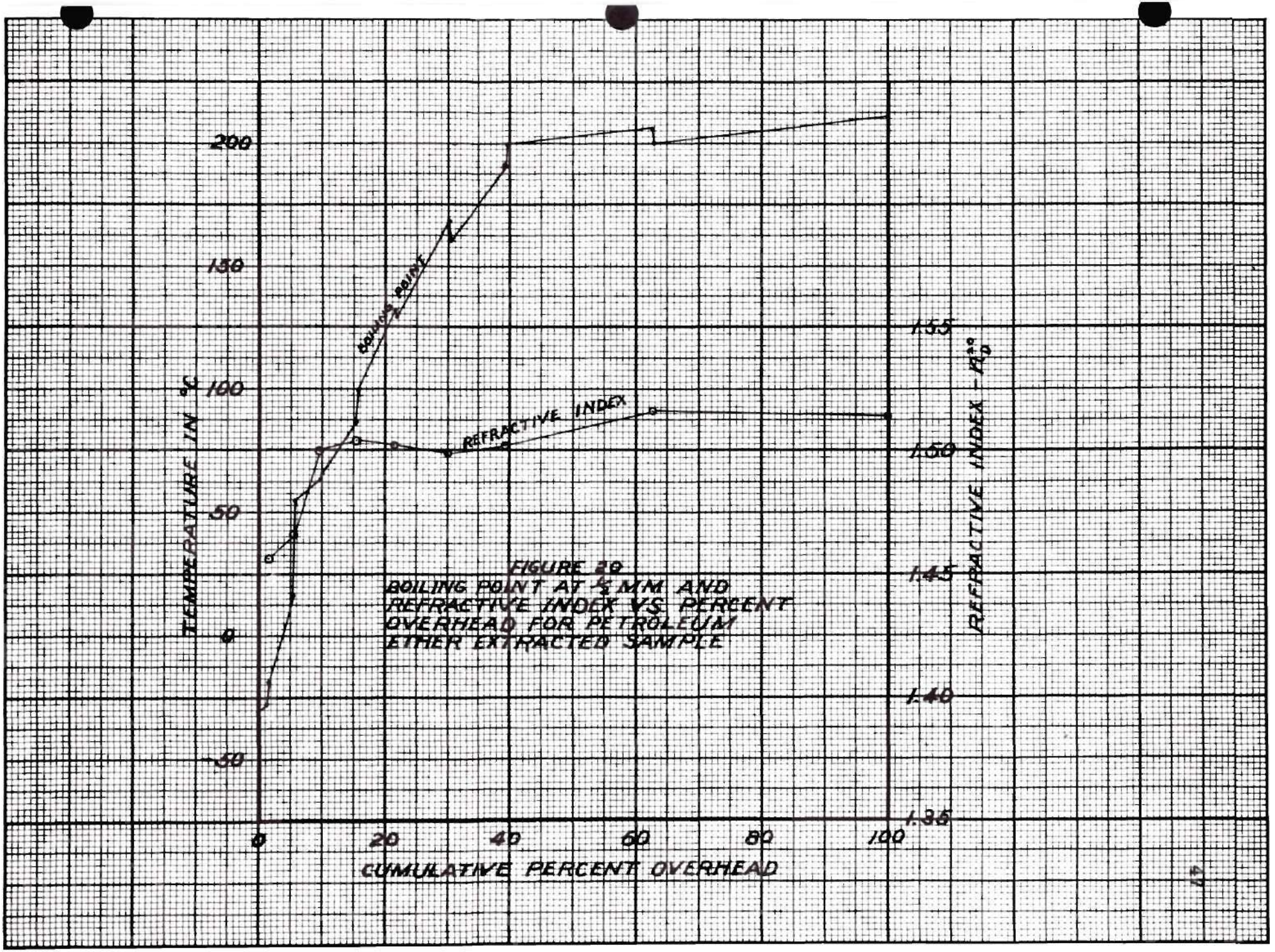


FIGURE 20
BOILING POINT AT 4 MM AND REFRACTIVE INDEX VS. PERCENT OVERHEAD FOR PETROLEUM ETHER EXTRACTED SAMPLE

FORM 5000
THE GEORGIA TECH COLLEGE INN

APPENDIX II

TABLES

TABLE III: EXTRACTION RATE DATA FOR RUNS 7, 8, AND 17

Run 7, Acetone Solvent, Weight of Needles - 15.7 Grams

Sample Number	Extraction Time in Minutes	Cumulative Ext. Time in Minutes	Extraction Cycles	Cumulative Extraction Cycles	Extract Weight in Grams	Percent Extract	Cumulative Percent Extract
1	31	31	2	2	0.735	4.68	4.68
2	94	125	6	8	0.258	1.64	6.32
3	64	189	5	13	0.165	1.05	7.67
4	106	295	7	20	0.035	0.22	7.89
5	136	431	15	35	0.041	0.26	8.15
6	157	588	-	-	0.069	0.44	8.59
Run 8, Acetone Solvent, Weight of Needles - 13.1 Grams							
1	28	28	2	2	0.680	5.20	5.20
2	96	124	6	8	0.193	1.47	6.67
3	65	189	5	13	0.110	0.84	7.51
4	105	294	7	20	0.033	0.25	7.76
5	137	431	16	36	0.039	0.30	8.06
6	149	580	-	-	0.057	0.44	8.50

TABLE III, continued

Run 17, Acetone Solvent, Weight of Needles - 12.7 Grams

Sample Number	Extraction Time in Minutes	Cumulative Ext. Time in Minutes	Extraction Cycles	Cumulative Extraction Cycles	Extract Weight in Grams	Percent Extract	Cumulative Percent Extract
1	19	19	1	1	0.517	4.07	4.07
2	13	32	1	2	0.113	0.89	4.96
3	107	139	11	13	0.139	1.09	6.05
4	159	298	15	28	0.101	0.80	6.85
5	364	662	-	-	0.036	0.28	7.13

TABLE IV: EXTRACTION RATE DATA FOR RUNS 9 AND 10

Run 9, Petroleum Ether Solvent, Weight of Needles - 14.6 Grams

Sample Number	Extraction Time in Minutes	Cumulative Ext. Time in Minutes	Extraction Cycles	Cumulative Extraction Cycles	Extract Weight in Grams	Percent Extract	Cumulative Percent Extract
1	22	22	2	2	0.305	2.09	2.09
2	85	107	7	9	0.077	0.53	2.62
3	105	212	11	20	0.027	0.18	2.80
4	82	294	7	27	0.039	0.27	3.07
5	151	445	-	-	0.018	0.12	3.19
6	409	854	-	-	0.032	0.22	3.41

Run 10, Petroleum Ether Solvent, Weight of Needles - 14.3 Grams

1	22	22	2	2	0.284	1.99	1.99
2	87	109	7	9	0.070	0.49	2.48
3	103	212	11	20	0.027	0.18	2.66
4	83	295	7	27	0.035	0.25	2.91
5	150	445	-	-	0.016	0.11	3.02
6	409	854	-	-	0.028	0.20	3.22

TABLE V: EXTRACTION RATE DATA FOR RUNS 11, 12, AND 18

Run 11, Benzene Solvent, Weight of Needles - 13.5 Grams

Sample Number	Extraction Time in Minutes	Cumulative Ext. Time in Minutes	Extraction Cycles	Cumulative Extraction Cycles	Extract Weight in Grams	Percent Extract	Cumulative Percent Extract
1	40	40	1	1	0.583	4.31	4.31
2	48	88	2	3	0.132	0.98	5.29
3	41	129	3	6	0.034	0.25	5.54
4	62	191	6	12	0.026	0.19	5.73
5	200	391	23	35	0.019	0.14	5.87
6	398	789	-	-	0.010	0.07	5.94

Run 12, Benzene Solvent, Weight of Needles - 14.0 Grams

1	40	40	1	1	0.545	3.89	3.89
2	43	83	2	3	0.124	0.89	4.78
3	48	131	3	6	0.030	0.21	4.99
4	71	202	6	12	0.021	0.15	5.14
5	205	407	24	36	0.016	0.11	5.25
6	398	805	-	-	0.008	0.06	5.31

TABLE V, continued

Run 18, Benzene Solvent, Weight of Needles - 12.0 Grams

Sample Number	Extraction Time in Minutes	Cumulative Ext. Time in Minutes	Extraction Cycles	Cumulative Extraction Cycles	Extract Weight in Grams	Percent Extract	Cumulative Percent Extract
1	13	13	1	1	0.435	3.63	3.63
2	18	31	1	2	0.077	0.64	4.27
3	106	137	11	13	0.071	0.59	4.86
4	164	301	14	27	0.040	0.33	5.19
5	345	646	-	-	0.008	0.07	5.26

TABLE VI: EXTRACTION RATE DATA FOR RUNS 13 AND 14

Run 13, Isopropyl Alcohol Solvent, Weight of Needles - 13.1 Grams

Sample Number	Extraction Time in Minutes	Cumulative Ext. Time in Minutes	Extraction Cycles	Cumulative Extraction Cycles	Extract Weight in Grams	Percent Extract	Cumulative Percent Extract
1	21	21	1	1	0.665	5.08	5.08
2	36	57	1	2	0.105	0.78	5.86
3	95	152	5	7	0.127	0.97	6.83
4	83	235	6	13	0.098	0.75	7.58
5	153	388	13	26	0.086	0.66	8.24
6	368	756	-	-	0.113	0.86	9.10

Run 14, Isopropyl Alcohol Solvent, Weight of Needles - 12.8 Grams

1	19	19	1	1	0.660	5.16	5.16
2	34	53	1	2	0.112	0.88	6.04
3	94	147	5	7	0.109	0.85	6.89
4	83	230	6	13	0.088	0.69	7.58
5	152	382	13	26	0.081	0.63	8.22
6	365	747	-	-	0.104	0.81	9.03

TABLE VII: EXTRACTION RATE DATA FOR RUNS 15 AND 16

Run 15, Methyl Ethyl Ketone Solvent, Weight of Needles - 13.1 Grams

Sample Number	Extraction Time in Minutes	Cumulative Ext. Time in Minutes	Extraction Cycles	Cumulative Extraction Cycles	Extract Weight in Grams	Percent Extract	Cumulative Percent Extract
1	17	17	1	1	0.560	4.28	4.28
2	24	41	1	2	0.095	0.73	5.01
3	87	128	9	11	0.110	0.84	5.85
4	121	249	13	24	0.052	0.40	6.25
5	73	322	7	31	0.021	0.16	6.41
6	476	798	-	-	0.069	0.53	6.94

Run 16, Methyl Ethyl Ketone Solvent, Weight of Needles - 14.4 Grams

1	12	12	1	1	0.675	4.69	4.69
2	26	38	1	2	0.121	0.84	5.53
3	86	124	9	11	0.133	0.92	6.45
4	119	243	15	26	0.060	0.42	6.87
5	65	308	7	33	0.023	0.16	7.03
6	469	777	-	-	0.086	0.60	7.63

TABLE VIII

AVERAGE PERCENT TOTAL EXTRACT VS. TIME

Extraction with Acetone:

Time in Minutes	Average Percent Pine Needle Weight	Average Percent Total Extract (Based on 100% at 600 minutes)
30	4.83	59.8
50	5.25	65.0
100	6.01	74.5
150	6.36	78.8
200	7.22	89.4
300	7.51	93.0
400	7.72	95.6
500	7.90	97.8
600	8.08	100.0

Extraction with Petroleum Ether:

30	2.07	64.7
50	2.22	69.4
100	2.48	77.5
150	2.71	84.6
200	2.86	89.4
300	3.00	93.8
400	3.07	95.9
500	3.13	97.8
600	3.20	100.0

Extraction with Benzene:

50	4.36	79.7
100	4.99	91.1
150	5.24	95.7
200	5.30	96.9
300	5.37	98.2
400	5.41	99.0
500	5.45	99.6
600	5.47	100.0

TABLE VIII, continued

Extraction Isopropyl Alcohol:

Time in Minutes	Average Percent Pine Needle Weight	Average Percent Total Extract (Based on 100% at 600 minutes)
30	5.33	60.5
50	5.72	65.0
100	6.42	72.8
150	6.99	79.3
200	7.36	83.5
300	7.90	89.6
400	8.29	94.0
500	8.58	97.5
600	8.81	100.0

Extraction with Methyl Ethyl Ketone:

30	4.82	68.4
50	5.38	76.4
100	5.98	84.9
150	6.25	88.6
200	6.44	91.3
300	6.68	94.8
400	6.81	96.6
500	6.93	98.3
600	7.05	100.0

TABLE IX

AVERAGE PERCENT TOTAL EXTRACT VS: EXTRACTION CYCLES

Extraction with Acetone:

Extraction Cycles	Average Percent Pine Needle Weight	Average Percent Total Extract (Based on 100% at 25 Cycles)
2	4.89	65.0
5	5.60	74.5
10	6.56	87.3
15	7.17	95.4
20	7.38	98.1
25	7.52	100.0

Extraction with Petroleum Ether:

2	1.99	68.2
5	2.37	81.2
10	2.58	88.4
15	2.69	92.1
20	2.80	95.9
25	2.92	100.0

Extraction with Benzene:

1	3.94	73.4
2	4.58	85.3
5	4.95	92.1
10	5.17	96.3
15	5.26	98.0
20	5.33	99.2
25	5.37	100.0

Extraction with Isopropyl Alcohol:

1	5.10	62.5
2	5.90	72.3
5	6.54	80.1
10	7.25	88.8
15	7.68	94.1
20	7.84	96.0
25	8.16	100.0

TABLE IX, continued

Extraction with Methyl Ethyl Ketone:

Extraction Cycles	Average Percent Pine Needle Weight	Average Percent Total Extract (Based on 100% at 25 Cycles)
1	4.44	67.9
2	5.22	79.9
5	5.77	88.3
10	6.10	93.4
15	6.25	95.6
20	6.40	97.9
25	6.54	100.0

TABLE X: DISTILLATION OF ACETONE EXTRACT

Distillation of 49.01 Gram Sample Extracted With Acetone

Sample Number	Oil Bath T.° C	Column Wall T.° C	Distillation Temp.° C	Pressure mm. Hg.	Weight of Distillate in Grams	Refractive Index $n_d^{20°}$	Appearance of Distillate
1	145	30	--	10	1.331	1.3731	clear, colorless, two phases
2	170	30	--	30 to 2	0.199	1.3884*	clear, yellow
3	170	160	80 to 87	1/2	0.306**	1.5066	clear, amber
					0.084	1.4883	clear, dark amber
4	210	206	98 to 135	3/4	0.389	1.5050	slightly cloudy, amber
5	230	206	130 to 168	2 to 1 1/2	0.954	1.5031	slightly cloudy, dark amber
6	240	220	158 to 180	1 1/2	1.060	1.5088	clear, red amber
7	direct flame	224	160 to 185	1 1/2 to 3	4.499**	1.5019	thick, dark red, cloudy
					0.287	1.4892	clear, dark red

* Extrapolated (High range precision refractometer)

** The larger part of the distillate collected in the neck of the condenser. The smaller portion condensed in the condenser and collected in the end of the condenser tube.

TABLE XI: DISTILLATION OF PETROLEUM ETHER EXTRACT

Distillation of 47.84 Gram Sample Extracted With Petroleum Ether

Sample Number	Oil Bath T.°C	Column Wall T.° C	Distillation Temp.° C	Pressure mm. Hg.	Weight of Distillate in Grams	Refractive Index $n_d^{20°}$	Appearance of Distillate
1	140	27	30 to 32	25	0.145	1.4563	clear, colorless
2	150	128	30 to 40	12 to 2	0.348	1.4659	clear, colorless
3	190	135	72 to 82	1 1/2	0.405	1.5002	clear, lt. yellow
4	210	172	79 to 100	1	0.479	1.5045	clear, yellow
5	240	208	100 to 132	1/2	0.549	1.5015	clear, yellow
6	260	222	129 to 168	1/2	0.791	1.4981	clear, amber
7	270	226	160 to 190	1/2	0.851	1.5026	cloudy, amber
8	280	256	160 to 206	1/2	2.412	1.5162	syrupy, cloudy, amber
9	287	286	200 to 212	1/2	3.073	1.5141	syrupy, cloudy, amber

TABLE XII: DATA FOR PLOTTING FIGURE 19

Distillation of 49.01 Gram Sample Extracted With Acetone

Sample Number	Pressure mm. Hg	Distillation Temp. in °C	Estimated Distillation Temp. at 1/2 mm. Hg by Cox Chart	Refractive Index	% Overhead	Cumulative Overhead*
1	10	--	--	1.3731	15.2	15.2
2	30 to 2	--	--	1.3884**	2.3	17.5
3	1/2	80 to 87	80 to 87	1.5066	3.5	21.0
4	3/4	98 to 135	92 to 126	1.5050	4.5	25.5
5	2 to 1 1/2	130 to 168	104 to 143	1.5031	10.9	36.4
6	1 1/2	158 to 180	135 to 157	1.5088	12.1	48.5
7	1 1/2 to 3	160 to 185	137 to 162	1.5019	51.5	100.0

* Where two products were obtained at one range of distillation, the smaller, evidently a product of pyrolysis, is omitted in the calculation of percent overhead.

** Extrapolated

TABLE XIII: DATA FOR PLOTTING FIGURE 20

Distillation of 47.84 Gram Sample Extracted With Petroleum Ether

Sample Number	Pressure mm. Hg	Distillation Temp. in °C	Estimated Distillation Temp. at 1/2 mm. Hg by Cox Chart	Refractive Index	% Overhead	Cumulative Overhead
1	25	30 to 32	-30 to -28	1.4563	1.6	1.6
2	12 to 2	30 to 40	-19 to +17	1.4659	3.8	5.4
3	1 1/2	72 to 82	55 to 64	1.5002	4.5	9.9
4	1	79 to 100	66 to 87	1.5045	5.3	15.2
5	1/2	100 to 132	100 to 132	1.5015	6.1	21.3
6	1/2	129 to 168	129 to 168	1.4981	8.7	30.0
7	1/2	160 to 190	160 to 190	1.5026	9.5	39.5
8	1/2	200 to 206	200 to 206	1.5162	23.3	62.8
9	1/2	200 to 212	200 to 212	1.5141	37.2	100.0

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